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COLLOID CHEMISTRY IN CERAMICS*

By E. A. Hauser

Introduction

Mr. Chairman, Fellows of The American Ceramic Society, Members, and guests! I consider it a great honor to have been invited to deliver before this gathering the Edward Orton, Jr., Memorial Lecture for 1941. That your choice has fallen on me, neither a ceramist by profession nor a specialized ceramic chemist or physicist, makes me even more proud, and I therefore want to thank you from the bottom of my heart.

I come here not to offer you a lecture on recent developments in ceramics, a topic which undoubtedly will be handled in the course of your Meeting by more competent men, but to lay before you in simple form a few fundamental colloid chemical and physical concepts which have a direct bearing on basic problems in ceramics.

This consideration of why and where colloid chemical reasoning and research have become a science indispensable for progressive developments in ceramics is the greatest tribute to the memory of Edward Orton, Jr., who pioneered in the United States in the importance of scientific research in ceramics.

I. Colloids and the Colloidal State

Colloids will first be defined largely by telling what they are not. Experience shows that many persons still believe that colloids are tiny particles floating around in a fluid medium. Colloids may not be considered as a special group of substances but rather as a special state of matter. It is a state in which matter exhibits specific properties that are not predictable from those which the same matter exhibits either as coarse-solid or in solution. The primary characteristic of the colloidal state is the dimensional range between 500 and 1 mμ.† It is the world of these dimensions which has been too long neglected. Inasmuch as matter in general may be considered tridimensional, a substance will exhibit colloidal properties in relation to its thickness only if this dimension has been reduced to the colloidal range (gold leaf); if thickness and width are of colloidal dimensions, the substance will be a colloid in relation to these two but not to its length (fine fibers). Only if all three dimensions fall in the foregoing range is a corpuscular colloidal particle or a colloidal dispersion (gold sol) being considered.

How may the fact be explained that matter in the colloidal state is generally far more reactive than it is in any other form? Consider for this purpose a large cube composed of (+) and (−) ions (ionic lattice), for example, a bromargyrite (silver bromide) crystal. A silver ion located in the center is surrounded equidistantly by six bromine ions or a bromine ion by six silver ions; but a silver or bromine ion located in the center of a surface plane is surrounded by only five, one located in an edge by four and one in a corner position by only three (Fig. 1). Chemically speaking, all of the ions except those located in the center are not fully saturated and will therefore tend to reach equilibrium by adsorbing, respectively, (+) or (−) charges from their environment. Such adsorption is the necessary prelude to reactions. It now becomes self-evident that, by decreasing the size of the particle, the reactivity is increased because the number of such preferential spots per unit area of surface is increased. This change may also be expressed in terms of energy. The total energy of a body of matter may be considered to be the sum of its inner energy and its surface energy. The latter is due to the forces emanating from the ultimate building units located in it to a depth of colloidal dimensions.

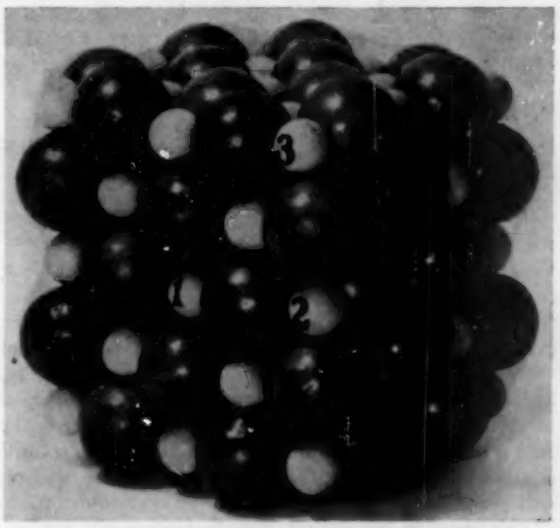


Fig. 1.—Close-packed model of a bromargyrite crystal. The silver atom, 1, is surrounded by five bromine atoms; only four are visible, the fifth being located behind the silver atom; silver atom, 2, is surrounded by four and silver atom, 3, by three bromine atoms (all are visible in the model).

When the corpuscular particle has been reduced to colloidal size, its surface energy will be predominant, its inner energy having become insignificant in comparison. That fact also explains why colloid chemistry is frequently called the chemistry of surfaces or surface reactions. Upon further comminution, the term "surface" as generally used becomes meaningless because

* The Edward Orton, Jr., Memorial Lecture presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., March 31, 1941.

† 1 mμ = 10^{-7} cm.

the dimensions of the ultimate building units of matter themselves have now been reached.

If the silver bromide particle is now assumed to be suspended or dispersed in water containing a dissociated electrolyte (for example, silver nitrate), the silver ions will be preferentially attracted by the bromine ions located in the surface of the crystal forming insoluble AgBr. The particle thereby acquires a net (+) charge (Fig. 2). The NO_3^- ions form the counterions, and what is known as a diffuse electric double layer has been set up around the particle. The concentration and stand-off distance of the counterions control the stability of the suspension. If all available Br^- spots on the surface have been taken care of by Ag^+ ions, the particle will have acquired a maximum positive charge and will offer maximum repulsion to other particles

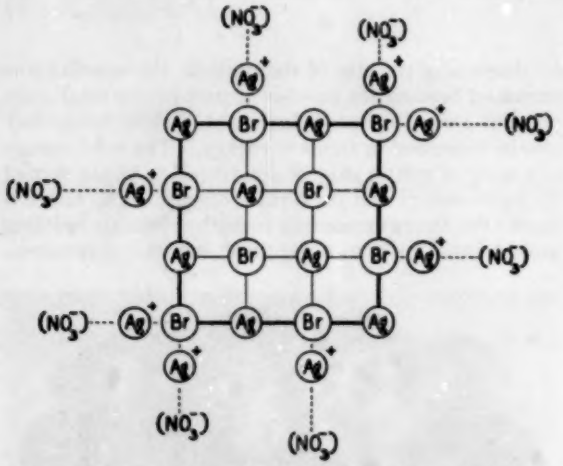


FIG. 2.—Ionic arrangement in diffuse electric double layer resulting in positive-charged silver bromide particle (schematic and simplified).

carrying the same charge. If excess $AgNO_3$ is present, the counterions are crowded into the double layer, eventually neutralizing some of the surface charge and thereby decreasing the stability of the suspension (Fig. 3). If the silver bromide was formed in the presence of an excess of KBr, the bromine (−) will adsorb on the Ag^+ spots (the reaction leading to the least soluble compound) and a negatively charged particle will result (Fig. 4).

The speaker hopes that this discussion has emphasized the importance of surface development, surface energy, and surface reactivity because it is this phase of colloid chemistry that is of primary importance in ceramics and because it is through the application of these necessary colloidal concepts that a better understanding may be obtained of the properties of the ceramic raw material, the clay minerals.

The discovery that matter present in crystalline form diffracts X rays in an organized pattern made it possible to prove that the clay minerals, many of which had previously been considered amorphous, actually are crystalline in structure. Systematic studies furthermore revealed that although members of the kaolinite group give the same composition by chemical analysis, they yield different X-ray patterns, whereas members of the montmorillonite group differ in chemical analysis but give approximately the same X-ray diffraction pattern (Table I). It soon became evident that the great variations in properties of the various clay minerals could be accounted for only if they were assumed to be basically composed of comparatively simple building units and that their differences were largely due to the manner in which these units were put together. These structures in a way might be compared with brick houses. All kinds can be built and the same brick and the same mortar may be used to bind them together. What are the brick in building clay minerals? The first type is the combination of one silicon atom with four oxygen atoms to form a silicon-oxygen tetrahedron (Fig. 5, *left*). The second type is the combination of one aluminum or magnesium atom with six

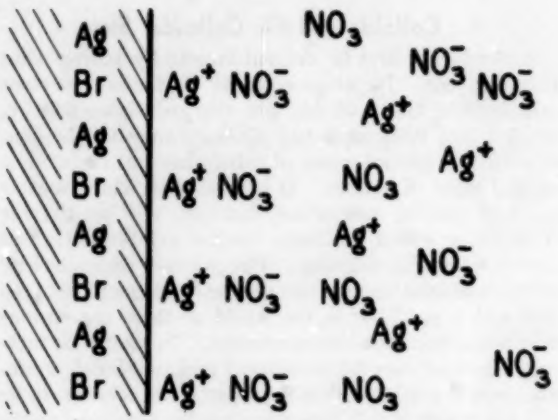


FIG. 3.—Ionic arrangement in electric double layer in presence of excess electrolyte; state of discharge (schematic).

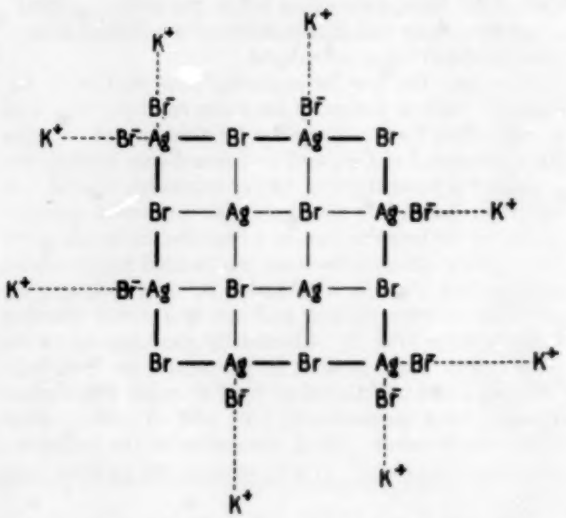


FIG. 4.—Ionic arrangement in diffuse electric double layer resulting in negative-charged silver bromide particle (schematic and simplified).

TABLE I
THE CLAY MINERALS

Group	Mineral	Chemical composition	Type of crystal lattice
Kaolin	Kaolinite Dickite Nacrite Halloysite	$Al_4(Si_4O_{10})(OH)_8$	Kaolinite (Dickite)* (Nacrite)* Kaolinite
	Hydrohalloysite	$Al_4(Si_4O_6)(OH)_{10}$	Hydrohalloysite
Montmorillonite	Pyrophyllite	$Al_4(Si_8O_{20})(OH)_4$	Montmorillonite
	Talc	$Mg_6(Si_8O_{20})(OH)_4$	
	Montmorillonite	$Al_4[Mg](Si_8O_{20})(OH)_4 \cdot xH_2O$†	
	Nontronite	$Fe_4^{+++}[Mg](Si_8O_{20})(OH)_4 \cdot xH_2O$†	
	Beidellite	$Al_4[Mg](Si_8[Al]O_{20})(OH)_4 \cdot xH_2O$†	
	Saponite	$Mg_6(Si_8[Mg]O_{20})(OH)_4 \cdot xH_2O$†	
Hydromica	Illite	$Ky \cdot Al_4[Fe_2^{+++}Mg](Si_{8-y} \cdot [Aly] \cdot O_{20}(OH)_4$‡	Illite
Mica	Muscovite	$K_2 \cdot Al_6(Al_2Si_6O_{20})(OH)_4$	Mica

* It is questionable if minute differences in the X-ray diffraction pattern of kaolinite, dickite, and nacrite justify a separate classification for the structure of the latter two minerals.
† Symbols in [ ] indicate that they may substitute for the symbol written to the left of the bracket.
‡ Only when $y = 2$ and no substitution for the aluminum exists is this formula transformed into that of muscovite.

oxygen atoms to form an aluminum or magnesium-oxygen octahedron (Fig. 5, *right*). What is the mortar? The chemical valences. These may also be expressed by the distribution of electrons throughout the system.

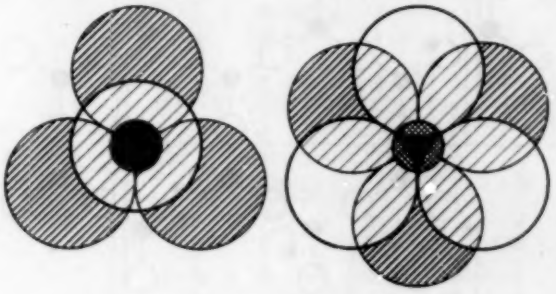


FIG. 5 (*left*).—Silicon-oxygen tetrahedron (schematic) representing top view of the model. The oxygen atom on top has been drawn as a transparent sphere to show the location of the silicon atom in the cavity formed by the four oxygens; (*right*) aluminum-(magnesium) oxygen octahedron (schematic); the oxygen atoms constituting the upper layer have been drawn transparent to show the location of the aluminum or magnesium atom in the cavity formed between the two oxygen (hydroxyl) layers.

A silicon atom is known to share four electrons with neighboring atoms (Table II). But each oxygen atom needs two electrons for saturation. The silicon-oxygen tetrahedron as pictured therefore is not saturated. If the oxygen atoms are replaced with hydroxyl groups, the tetrahedron then is saturated because each hydroxyl needs only one electron. Thus, by sharing the right number of electrons, two or more atoms are firmly held together; in this specific case, reference is generally made to a chemical bond or a covalent bond.

If several silicon-oxygen tetrahedra are combined so that two always share one oxygen, a chainlike structure results. In such a chain, two of the oxygen atoms belonging to one silicon atom remain unsaturated. This deficiency may be compensated by attaching a sodium atom to every unsaturated oxygen. A fibrillar aggregate is thus formed, which, if dispersed in water, represents the structure of sodium silicate or water glass (Fig. 6). The fact that the sodium ion hydrates appreciably and the presence of such long-chain aggregates offer a simple explanation for the solubility of sodium silicate and the high viscosity of its solutions. The entanglement of these fibrillar aggregates on desiccation also explains the formation of coherent sodium-

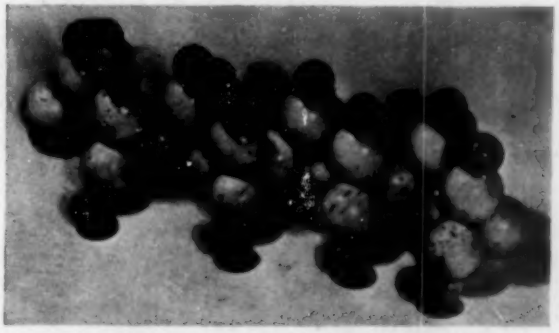


FIG. 6.—Model of a sodium-silicate chain (theoretical); white balls represent oxygen atoms; smaller black balls, sodium atoms (diameters of balls in correct proportions).

TABLE II
SHARING OF ELECTRONS BETWEEN ATOMS

The number at the right of the chemical symbol corresponds to the number of available or needed electrons; + sign indicates that the atom or group gives electrons; − sign, that it takes electrons.

Nonmetallic atoms or groups	Polyvalent metallic atoms	Monovalent metallic atoms
Oxygen − 2	Silicon + 4	Sodium + 1
Hydroxyl − 1	Aluminum + 3	Potassium + 1
	Iron (ferric) + 3	Hydrogen + 1
	Magnesium + 2	

silicate films. Their structure is comparable to films obtained from long-chain high molecular organic compounds, for example, rubber or cellulose. If sodium silicate is reacted in solution with a solution of an acid, the sodium will exchange for the acid hydrogen, thus forming a silicic acid chain (Fig. 7). If two or more of these chains come close together or tangle up, condensation between neighboring hydroxyl groups occurs.

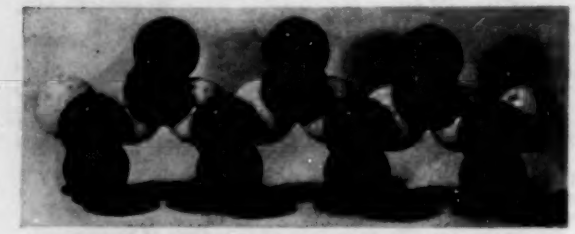


FIG. 7.—Model of a silicic acid chain (theoretical), top view; white balls represent oxygen atoms; black balls, hydroxyl groups.

Water is split off and the chains are now held together by shared oxygen atoms. A loose, *unoriented*, but nevertheless rigid tridimensional structure results, and a hydrous silica gel has been formed (Fig. 8). If silicon-oxygen tetrahedra are joined to a *well-oriented* tridimensional structure, quartz, tridymite, or cristobalite are the result.

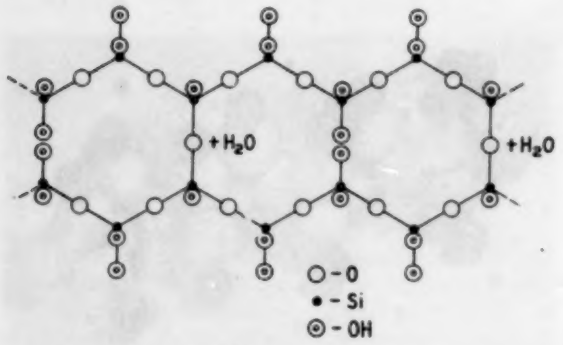


FIG. 8.—Formation of network structure by condensation (schematic).

In a consideration of the simple silicon-oxygen tetrahedra chain, just as it was possible to link two or more silicic acid chains together by condensation, two or more silicon-oxygen tetrahedra chains may be joined by having them share oxygen atoms (Fig. 9). A hexagonal network or silicon-oxygen sheet has thus been formed. If these hexagons are symmetrical, a sheet of crystalline structure results; if they are not symmetrically aligned, a silica glass is obtained (Fig. 10). Only the oxygen in the vertex position of every tetrahedron remains unsaturated. If this is replaced by a hydroxyl group, the sheet is perfectly saturated. (The predominance of surface in such sheets makes the effect of unsaturated edge or corner positions negligible.) Such a structure is known as a hydrated silica sheet (Table III(4)).

A similar sheet may be formed by joining together magnesium-oxygen octahedra. If all of the remaining unsaturations are saturated with hydrogen, there are two layers of hydroxyl groups, each in hexagonal closest packing and magnesium atoms sandwiched between. Inasmuch as six hydroxyl groups share three magnesium atoms in this arrangement, the layer lattice is saturated (except for the edge and corner points of the sheets) because one magnesium atom can share two electrons with neighboring atoms or groups. Several such neutral sheet parcels can be held together by weak secondary forces between opposed hydroxyl sheets. It must be noted, however, that the hexagonal symmetry of the individual sheet is lost when two are superimposed to form a double sheet held together by magnesium or

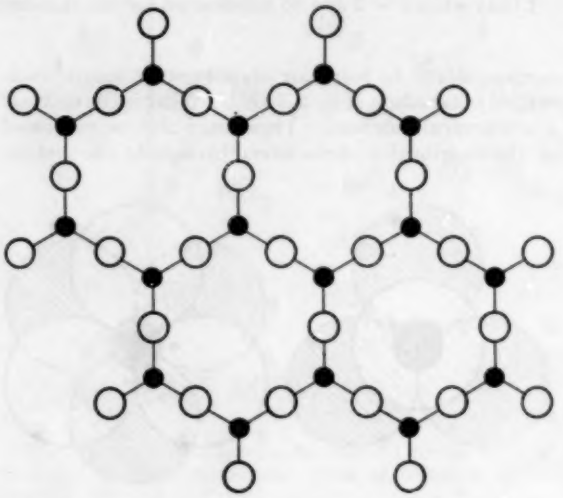


FIG. 9.—Structure of a symmetrical silicon-oxygen sheet (schematic); after W. H. Zachariasen, *Jour. Amer. Chem. Soc.*, **54**, 3841 (1932); only one plane shown.

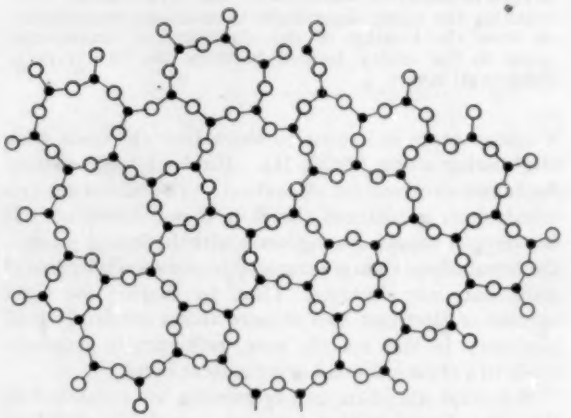
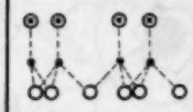
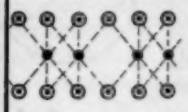
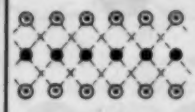
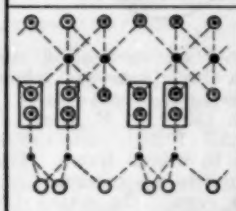
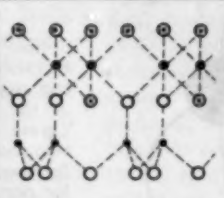
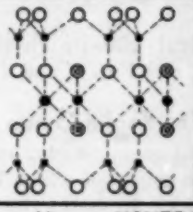
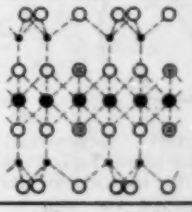
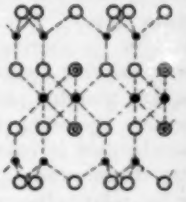
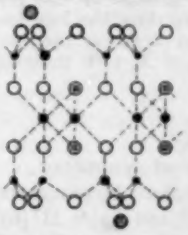
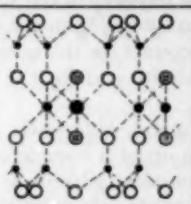


FIG. 10.—Structure of an unsymmetrical silicon-oxygen sheet; silica glass (schematic); after W. H. Zachariasen, *loc. cit.*; only one plane shown.

TABLE III

STRUCTURAL DATA OF CLAY MINERALS

The schematic drawings in the first columns represent the composition of the unit cell of the crystal lattice. All atoms are projected into one plane. The second column gives the number and type of atom or group in every lattice plane. The third column reveals the amount of available or needed electrons in every sheet. (See Table I.) If the (+) and (−) in this column compensate each other, the crystal is electrically neutral. If they do not, the lattice carries either a positive or negative charge. As the plus and minus charges are listed for every layer, it is easy to determine where the unbalance actually occurs in the lattice.

1 - SILICON TETRAHEDRON		
	1 O 1 Si 3 O	−2 +4 −6
2 - ALUMINUM OCTAHEDRON		
	3 OH 1 Al 3 OH	−3 +3 −3
3 - MAGNESIUM OCTAHEDRON		
	3 OH 1 Mg 3 OH	−3 +2 −3
4 - HYDRATED SILICA		
	4 OH 4 Si 6 O	−4 +16 −12
5 - GIBBSITE		
	6 OH 4 Al 6 OH	−6 +12 −6
6 - BRUCITE		
	6 OH 6 Mg 6 OH	−6 +12 −6
7 - HALLOYSITE		
	6 OH 4 Al 6 OH 4 OH 4 Si 6 O	−6 +12 −6 −4 +16 −12
8 - KAOLINITE		
	6 OH 4 Al 4 O 2 OH 4 Si 6 O	−6 +12 −10 +16 −12
• − Si • − Al ● − Mg ○ − O ⊛ − OH		
9 PYROPHYLLITE AND MONTMORILLONITE (IDEAL CASE)		
	6 O 4 Si 4 O + 2 OH 4 Al 4 O + 2 OH 4 Si 6 O	−12 +16 −10 +12 −10 +16 −12
10 TALC		
	6 O 4 Si 4 O + 2 OH 6 Mg 4 O + 2 OH 4 Si 6 O	−12 +16 −10 +12 −10 +16 −12
11 NONTRONITE		
	6 O 4 Si 4 O + 2 OH 4 Fe^{+++} 4 O + 2 OH 4 Si 6 O	−12 +16 −10 +12 −10 +16
12 MICA (ILLITE)		
	1 K 6 O 3 Si + 1 Al 4 O + 2 OH 4 Al 4 O + 2 OH 3 Si + 1 Al 6 O 1 K	+1 −12 +15 −10 +12 −10 +15 −12 +1
13 MONTMORILLONITE (SUBSTITUTED)		
	6 O 4 Si 4 O + 2 OH 3 Al + 1 Mg 4 O + 2 OH 4 Si 6 O	−12 +16 −10 +11 −10 +16 −12
• − Si • − Al, Fe^{+++} ● − Mg ○ − O ⊛ − OH ● − K		

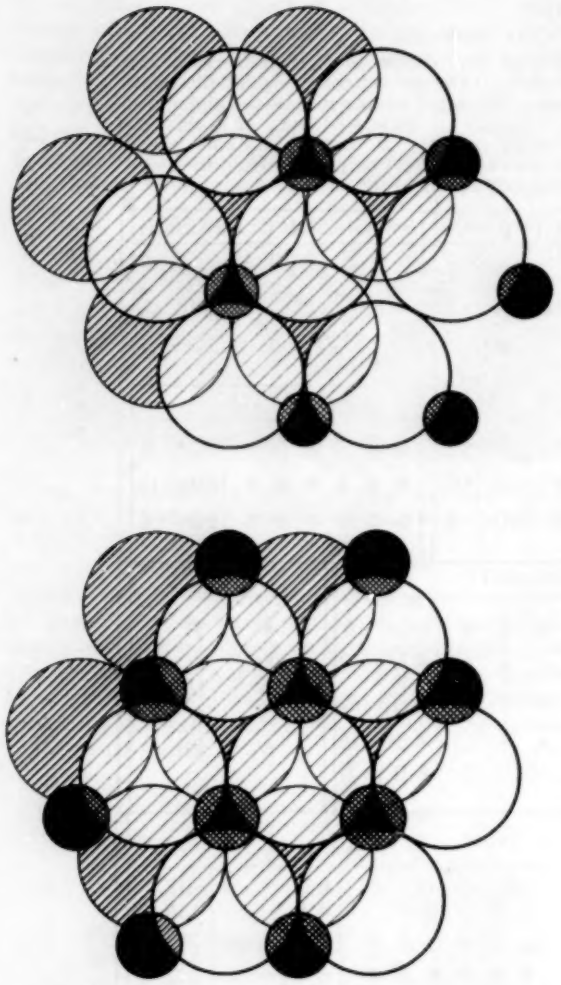


FIG. 11 (*bottom*).—Brucite $Mg(OH)_2$ (schematic); the hydroxyl groups constituting the upper layer have been drawn transparent so that the location of the magnesium atoms sandwiched between the two hydroxyl layers may be seen clearly. (*Top*) Gibbsite $Al(OH)_3$ (schematic); the hydroxyl groups in the top layer have been drawn transparent to show the location of the aluminum atoms sandwiched between the two staggered layers (compare positions of Al with those of Mg in bottom figure).

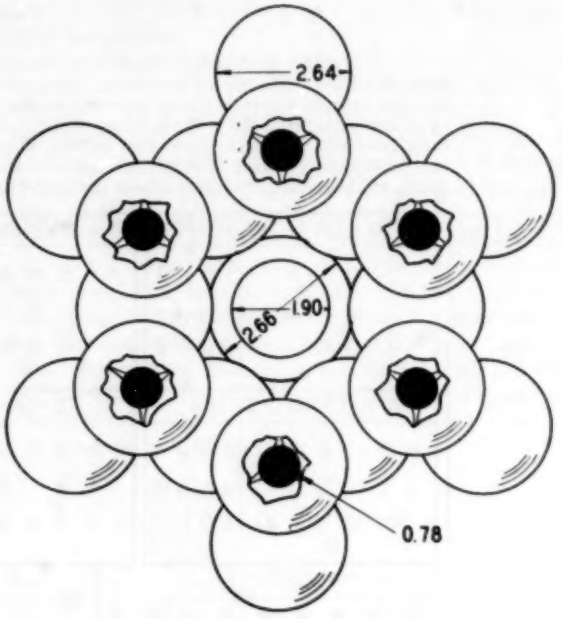


FIG. 12.—Hexagonal arrangement of silicon-oxygen tetrahedra in a silica sheet (top view, schematic); the top oxygens have been cut open to show the location of the silicon atoms (after P. F. Kerr, *Jour. Amer. Ceram. Soc.*, **21** [8] 267 (1938)); into the center space two concentric circles have been drawn. The larger one corresponds in diameter to a potassium atom, the smaller one to a sodium atom; the actual dimensions in Ångstrom units for the different atoms are indicated.

aluminum. The originally hexagonal symmetry of a single sheet is thus lowered to monoclinic by staggering the superimposed layers (see Fig. 11 and Table III(6)).

This refers to the mineral brucite, $Mg(OH)_2$. If aluminum is substituted for magnesium in the octahedra sheet, a neutral sheet can result only if one third of the places formerly occupied by magnesium remain vacant (aluminum shares three electrons to two of magnesium). This fact necessitates a slight change in the packing of the sheets. Otherwise there are again two hydroxyl sheets, this time with the aluminum atoms sandwiched in between. For reasons mentioned previously, these sheet parcels are somewhat more open-textured. The mineral, gibbsite (hydrargillite), $Al(OH)_3$, is now present (see Fig. 11 and Table III(5)).

II. The Kaolin Group

The most important group of clay minerals for the ceramist is the kaolin group of which kaolinite is the most common member. It shares the same chemical formula, $Al_4Si_4O_{10}(OH)_8$, with dickite and nacrite. In a unit parcel of kaolinite, a silica sheet is topped by a slightly distorted gibbsite layer. The silica sheet is joined to the gibbsite layer by sharing its tetrahedra vertices with it. The remaining hydroxyl groups of the adjoining gibbsite are thereby placed inside the hexagonal rings formed by the silica vertices (Table III(8)). The unit parcel again is balanced from the point of view of electron distribution. Several parcels may be held together by relatively strong secondary forces acting between the hydroxyl groups of one sheet facing the basal oxygens of the silica sheet in the other. The structure resulting from the staggering (mentioned before) also accounts for the nonexistence of very large crystals of kaolinite and for the vermicular forms frequently found.

The clay mineral, halloysite, another of the kaolin group, is made up of a complete hydrated silica sheet topped by a complete gibbsite layer. It thus happens that a particle exists, which in itself is held together by

secondary forces, that is, the bond between the adjacent hydroxyl groups of the hydrated silica and the gibbsite layer. Such a structure cannot be very stable. It is known that halloysite actually is very unstable toward elevated temperatures. At slightly above 40°C., the lattice begins to collapse. Condensation takes place until the ten hydroxyl groups in the center of the unit cell have split off four molecules of water, leaving four oxygens which act as a link between the silicon and aluminum sheets, plus two hydroxyls. A lattice identical with that of kaolinite results (Table III (7)).

III. The Montmorillonite Group

The next important group is generally known by the name of its most common member, montmorillonite. A particle is considered here which is composed of two silica sheets and a gibbsite layer sandwiched in between and joined to each other by shared oxygen atoms. The vertices of the silicon-oxygen tetrahedra, as in kaolinite, are directed toward the center. The remaining hydroxyl groups of the gibbsite layer again find their places in the hexagons formed by the vertices of the silicon-oxygen tetrahedra (Table III (9)). If the electron distribution in one unit cell is calculated, the parcel is neutral. Several parcels stacked together are held only by very weak secondary forces acting between the opposing oxygens of the silicon-oxygen tetrahedra.

Accurate analysis of montmorillonites, however, only occasionally will reveal a composition in accord with the ideal formula $(OH)_4Al_4Si_8O_{20}\cdot xH_2O$. Varying amounts of magnesium and iron are found chiefly and also variations in the Al to Si ratio. How can these differences be accounted for? If all of the aluminum ions in the gibbsite layer are replaced with ferric ions, no change has been made in the electronic balance of the structure. This mineral is known as nontronite (Table III (11)). An increase of aluminum over the ideal Al to Si ratio can be accounted for only by some replacement of Si^{++++} by Al^{+++} in the silica sheets. This seems to be true of the clay mineral, beidellite. (In the light of our present knowledge of the structure of the clay minerals, the classification of beidellite as a special clay mineral is no longer justified. Depending on the type of counterions associated with it and its swelling properties, it could be classified either as a substituted montmorillonite or as an illite.) If such a substitution occurs, the electronic balance of the silica sheets is destroyed and the sheet takes on a net negative charge (Table III (12)). The implications of this change in relation to certain properties will be discussed later. Magnesium likewise may be introduced as a substitute for aluminum in the gibbsite layer. As long as this substitution means only that the aluminum positions in the gibbsite layer are taken up by magnesium, the electron equilibrium will be upset. The center of the particle takes on a net negative charge (Table III (13)). The effect of this unbalance (as will be outlined) is different from the substitution discussed previously.

IV. The Illites

The next and last group to be considered are the illites. Their basic structure is similar to that of the ideal montmorillonite structure, that is, it consists of a gibbsite sheet joined by shared oxygens to a sheet of silicon-oxygen tetrahedra on each side. A considerable number of silicon atoms in the silica sheets, however, are replaced by aluminum atoms. Such a substitution, as previously mentioned, destroys the balance of electron distribution, resulting in silica sheets carrying a net negative charge. The fact that this negativity has its source very near the actual surface of the parcel causes the setting up of fairly strong attraction forces for (+) charges. K^+ ions generally will balance such excess charge and act as a bridge between adjacent parcels (Table III (12)). There seems to be good reason why potassium is found chiefly in the illites and in mica (muscovite) in preference to other alkali or earth alkali elements present in the soil or rocks. Of the common ions, it is the only one which, because of its size, cannot penetrate into the open hexagonal spaces of the oxygen layer of the silica sheet (Fig. 12). The K bond between parcels also prevents a parcel stack from being swelled by water entering in between the parcels as it can do in certain montmorillonites. The Al^{+++} in the gibbsite layer of the parcel occasionally will be replaced by Fe^{+++} without change in the electronic setup. The replacement of Al^{+++} by Mg^{++} may also be found in the gibbsite layer or the simple addition of Mg^{++} in brucite position. The results of such changes in the ideal illite structure are more or less identical with those occurring in altered montmorillonites to be discussed later in more detail.

FIG. 13.—Fibrillar aggregates (schematic); each crystallite (substituted montmorillonite) is composed of three staggered layers (OSi-OAlO-SiO).

A general formula for the various possible illites in analogy to those previously given may be written as $(OH)_4K_y(Al_4\cdot Fe_4\cdot Mg_4Mg_6)(Si_8-yAl_y)O_{20}$. If one fourth of the Si in the unit cell is replaced by Al, that is, if y assumes the figure 2 in the foregoing formula and if neither Fe nor Mg are present, the formula, $(OH)_4K_2Al_4(Si_6Al_2)O_{20}$ is obtained. This represents the unit cell of muscovite (mica), see Table III (12).

Thus there is really nothing mystic about the great variety of existing clay minerals, and their structure, if logically developed, is not as complex as many still believe. But by the same token it seems only logical to assume that really homogeneous deposits will be hard to find and that the large-scale consumer of clays is basing his work on the properties of a poorly defined mixture rather than on those of a well-defined single clay mineral, inasmuch as only slight differences in the basic structure of the minerals result in substantial changes of properties.

V. Properties of Clays Used in Ceramics

The following discussion therefore will refer to some of the properties of clays most important to ceramists in correlation with the structure of individual clay minerals. In doing so, the speaker hopes not so much to prove the vital importance of colloid chemistry in this field but to emphasize the serious need of systematic colloid chemical research as a basis for any successful future development in ceramics.

First of all, there is a significant difference between the compact corpuscular structure of a silver bromide crystal or a more open-textured cristobalite crystal and the assembly of sheets or layers in the clay minerals. Whereas the former could continue to grow under appropriate conditions in all three dimensions, the latter are limited both in size and shape. The various possible combinations of silicon-oxygen tetrahedra and aluminum or magnesium-oxygen octahedra layers, which have been discussed, result in parcels with a balanced electron distribution so that any further increase in size perpendicular to the plane of the sheets can be the result only of secondary and, therefore, of weak forces. Because the sheets themselves are held together by strong primary forces, any coherent growth must be limited to them. The logical result is easy cleavage between planes joined only by secondary forces and hence the formation of flaky crystals. The ease of cleavage depends on the bond holding the individual parcels together. The O–OH bond in kaolinite thus is materially stronger than the O–O bond in montmorillonite. This fact offers one explanation of why montmorillonite is capable of a higher degree of dispersion in water than is kaolinite. Illites, in accordance with their structure, will take up an intermediate position. An exception to this point of view seems to be the clay mineral, pyrophyllite. It has the same basic structure as an ideal montmorillonite, but, contrary to most montmorillonites which might be termed predominantly two-dimensional crystals, pyrophyllite exhibits perfect crystal growth in all three dimensions. No fully satisfactory answer so far is available. Pyrophyllite is a soft clay which can be easily comminuted by applying a shearing force; this would indicate that the neutral parcels are held together by secondary forces strong enough to withstand being pried apart by water. Such an assumption illustrates the importance of adsorbed, hydratable cations in providing means to overcome the secondary bonds between parcels and to permit easy dispersion. The other, less plausible, assumption is that the symmetry of the superimposed layers in pyrophyllite differs from montmorillonite in such a way that parcels are held together by shared oxygens. It might be noted here that a replacement of the gibbsite layer in pyrophyllite with a brucite layer results in the structure of the mineral, talc (Table III (10)).

The stability of suspended particles, as discussed at the outset, depends on the ability of the particles to form diffuse electric double layers. Just as a silver bromide particle formed by the reaction of stoichiometric proportions of silver nitrate and potassium bromide will, if suspended in pure water, remain uncharged although its surfaces may be considered as a patchwork of (+) and (−) charges with corresponding force fields emanating therefrom, so will all of the particles of those clay minerals which possess a balanced electron distribution be practically uncharged if they are suspended in pure water. The suspension would be unstable in such a condition for colliding particles will agglomerate because of molecular cohesion. If dissociated electrolytes, however, are present in the water, a diffuse electric double layer will form just as occurs if silver bromide is precipitated in the presence of excess electrolyte (see Figs. 2 and 4).

If kaolinite, which has a well-balanced neutral lattice, is considered first, a limited number of negative charges, theoretically may be adsorbed on the broken edges of the silicon and aluminum layers. Special considerations, which show that the silicon and aluminum atoms are embedded in cavities formed by the much larger oxygen or hydroxyl atoms, make this type of adsorption questionable. It is more probable, furthermore, that the adsorption of hydroxyl ions (if they are present in the dispersion medium) will take place on the basal oxygen sheet of the individual particle (see Table III (8)). This adsorption is preferential because of the high dipolar configuration of the hydroxyl ion, and, as a result, the particle takes on a net negative charge. Cations present in the dispersion medium will now function as counterions in the formation of the double layer. The building up of a net negative charge results in setting up a repulsive force for particles of equal sign. This, therefore, offers a simple explanation for the increased fluidity of kaolin suspensions with the addition of alkali because individual particles result in lower viscosity of a suspension than voluminous flocks or aggregates of uncharged particles.

As previously stated, not all of the atoms located in the edges or corners of the crystal sheets are saturated. It is only logical, therefore, to assume that adsorption on the "broken edges" will also take place. Even with very small crystal flakes, however, the adsorptive capacity due to such edges is small in comparison to adsorption on the surface of the sheets because they are of monoatomic thickness only. In the case of kaolinite, adsorption will be limited chiefly to the exposed oxygen layers of the basal silicon-oxygen tetrahedra. The strong OH–O bond between the crystallites (resulting in comparatively large particles) explains why the individual kaolinite particle or agglomerates of crystallites carry a comparatively weak net negative charge. This also explains the low stability of kaolin suspensions. The number of counterions is small. These counterions, chiefly alkali or earth alkali metals, are hydrated to varying degrees, and according to older concepts it is the hydration of the counterions which controls the thickness of the water film surrounding and separating the particles and controlling the viscosity and plasticity of the slip. It is impossible, however, to account for the measured thicknesses of water films solely by the hydration of the counterions. Not even could the added assumption that water molecules are adsorbed on the clay particle in oriented dipole fashion explain the measured distances of particles in plastic slips. The

presence of strongly adsorbed water films, furthermore, would demand a marked change in the viscosity of such immobilized water, which, however, so far has never been proved conclusively. Recent extensive work indicates more and more that the separation of the particles is due to an interaction between attractive and repulsive forces of a coulombic nature between the charges located in the surface of the particles and the surrounding counterions. Particle separation will depend on concentration, size, and shape of particles, on their net surface charge, and on the type, hydration, and concentration of the counterions. Type and hydration control their stand-off distance from the actual surface of the particle. As soon as the charge on the particle surface has reached its maximum, any further addition of electrolyte will tend to reduce the repulsive component of the total force acting between the particles until coagulation finally occurs.

Reductions in viscosity of a slip therefore result from an increase of the repulsive component. High viscosities are chiefly due to the formation of loose, bulky agglomerates, which retain in their interstices appreciable amounts of dispersion medium. Plasticity depends on an equilibrium between repulsive and attractive forces acting between the particles and the ions in the dispersion medium. Such equilibrium will assert itself while the particles are still at considerable distance from each other. Pure kaolinite, as previously pointed out, offers but little chance for adsorption of charging ions. Its plastic properties should not be very impressive. This has been proved by the study of plasticity of pure kaolinite of the usual particle size. It also follows, however, from the foregoing discussion that the plasticity of pure kaolinite slips must increase with decreasing particle size. Experiments correlating plasticity with particle size in kaolinite have fully confirmed this assumption.

The situation is entirely different with montmorillonites. As long as an ideal lattice (unaltered by substitution of atoms) is being considered, an increase in edge adsorbability must also be reckoned with owing to the presence of one more silica layer per crystallite over the kaolinite structure and an increased chance of hydroxyl adsorption caused by the presence of two oxygen sheets per crystallite. Such clays, therefore, will result in slips with "thicker water films," to use the old terminology. It must also be noted that this type of clay mineral will be more readily dispersed into smaller particles than kaolinite. A greater number of individual particles will therefore be present to contend with per unit weight in a given volume, thereby further increasing the surface area available for building up stabilizing diffuse electric double layers.

When "substituted" montmorillonite lattices are considered, the picture becomes more involved. If, for example, some of the aluminum of the gibbsite layer is replaced by magnesium, the center of the lattice as a whole becomes negatively charged. This charge increases with the number of aluminum positions in the gibbsite layer taken up by magnesium. Whereas Wyoming bentonite has a low substitution number, Death Valley clay has a very high number. Because the origin of this net negative charge is located in the center of the crystallite, its power of attraction for (+) charges will be considerably weakened at the surfaces of the parcels (see Table III (13)). It suffices, nevertheless, to adsorb cations loosely from the environment. The amount of adsorbable cations, expressed in milliequivalents per 100 gm. of clay, is generally known as the sorption or base-exchange capacity. From the foregoing data, it becomes evident that such clays, already possessing adsorbed cations, if placed in pure water can build up a double layer without the need of added electrolyte because the loosely held cations, on hydration, will dissociate to a certain distance from the surface of the particle and form the counterions of the diffuse double layer. Inasmuch as most of these counterions are adsorbed on the surfaces of the boundary sheets, they will tend, on hydration, to expand the distance between parcels held together loosely by the weak O–O bond. That this expansion actually occurs has been demonstrated by X-ray diffraction and by comparison of electrophoretic migration of various particle-size fractions. This prying apart of parcel agglomerates results not only in an extremely high degree of dispersion of the clay mineral, as previously mentioned, but also increases the free surface area and thereby the number of particles capable of building up double layers. This phenomenon, however, may also result in the reverse effect, the formation of fibrillar aggregates composed of individual flakes, which may be accounted for by the staggering of the layers as previously mentioned. Overlapping sheets will be loosely attracted by the dissociated counterions, which prevent contact of the parcels in the center parts of the opposing sheets (Fig. 13).

FIG. 14.—Microphotograph of desiccated bentonite (Alsifilm); after E. A. Hauser and D. S. le Beau, *Jour. Phys. Chem.*, **43**, 1037 (1939).

Upon desiccation of montmorillonite sols, the individual particles aggregate to such threads which interweave, thus forming a coherent, self-supporting structure (Fig. 14). This vermicular growth undoubtedly is due to the slight lattice displacement previously men-

tioned. Such self-supporting films still possess the properties of the clays from which they were prepared; for example, they will swell in water and revert to a sol. But if such films are treated with electrolytes having cations like potassium or larger, the individual crystallites are cemented together in a fashion similar to the structure of illites and mica. A water-insoluble, pure clay film, known as "Alsifilm," is the result. This example may well serve as proof of the importance of colloid chemical research in the study of the clay minerals.

The great sorption capacity of these clays, resulting from their unbalanced lattices, may be considered to be indicative of their strong surface charge. Depending on the type and amount of counterions present, these clays will therefore exhibit very pronounced plastic properties even at low concentration. The effect of dispersing agents is not so pronounced as with clays of the kaolin group because their particle size in a suspension is already at a minimum and the formation of a double layer is not dependent on adsorption of ions from the dispersion medium. From the discussion of plasticity and its causes, it becomes evident that larger quantities of water are needed in such systems than in nonplastic suspensions. The bonding strength and dry shrinkage increase with clays, which tends to produce plastic slips as does their dry strength.

The illites, in accordance with their structural characteristics, will take up positions intermediate between practically inert mica and highly plastic montmorillonites. The greater the replacement by aluminum of silicon in the tetrahedra sheets, the closer the illite will resemble genuine mica in its properties and the less plastic systems will it produce. The lower the degree of replacement in the silicon layer and the greater the substitution of magnesium for aluminum in the gibbsite layer, the more plastic a system will result.

VI. Base Exchange of Clay Minerals

In reference to the base exchange of the clay minerals, the fact has been established that the ultimate clay crystal carries a net negative charge, either by adsorption of anions on to its surface or because of an unbalanced crystal lattice. It may therefore be compared as a whole with a very complex anion. This anion has the ability to adsorb a certain number of cations to balance its charge. When the clay is suspended in water, these cations will dissociate to a distance which depends on their valency and hydration. The entire clay micelle may therefore be compared with a dissociated electrolyte. Just as sodium soap will exchange its sodium for the calcium in hard water, so may the cation of the clay be exchanged for another one. Most montmorillonites with an unbalanced gibbsite layer carry sodium ions as balancing counterions. Sodium is a monovalent ion. Many sodium ions are therefore needed to compensate the lattice charge and to eliminate the repulsive forces emanating therefrom. The considerable hydration of the sodium ions results in large distances between particles, thick water layers, a highly plastic system, and high, dry shrinkage and strength.

The high plasticity is due to the large separating distances; and the high dry strength, to the fact that charged particles, if forced to settle, have the ability to pack as closely as possible, whereas particles, already discharged, settle haphazardly, resulting in a loose and weak final structure (Fig. 15). By acid-washing the clay or submitting it to dialysis or electrodialysis, the sodium is exchanged for hydrogen, and an acid or hydrogen clay is produced. The hydrogen ion is monovalent but not hydrated. The "water films" will therefore be very thin, resulting in a sticky plastic system. As a logical consequence, the dry shrinkage of the system and its dry strength will be low. If the monovalent sodium ions are replaced with divalent calcium ions, a clay is produced which strikes a happy medium in its properties between the two just discussed because the hydration of calcium ion is intermediate between those of hydrogen and sodium.

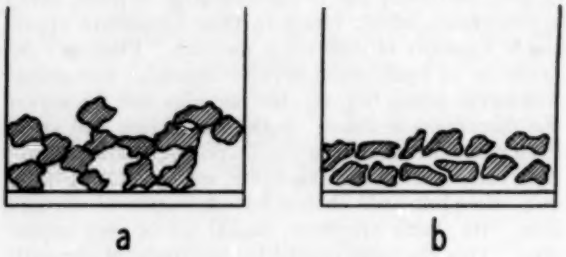


FIG. 15.—Sedimentation volume (schematic); (*a*) particles have been discharged before sedimentation, resulting in loose aggregates; (*b*) charged particles sediment and arrange themselves in such a way that a minimum of surface is exposed.

VII. Conclusions

This is the picture I have wanted to draw today. Even with the generous allotment of time, it can be only a sketch. I have tried to offer the facts on which I base my firm opinion that the ceramic industry can be controlled in every step and that ceramists can achieve further improvements and probably introduce entirely new methods of manufacture by applying colloid chemical reasoning. It must be remembered, however, that "it still is a long way to Tipperary." Long and possibly tedious systematic research is needed to obtain all data essential for perfect control of the various steps in the production of ceramic goods. First of all, perfectly pure and well-defined clay minerals must be obtained and studied from every possible angle, mineralogically, by X-ray diffraction, and by chemical analysis, in terms of particle size and particle-size distribution, viscosity, plasticity, and electric charge. When such data are available, studies may be made on mixtures of the different clay minerals in preselected proportions and so on until all possibilities are exhausted instead of working with ill-defined heterogeneous mixtures of clays and praying that things will go all right. It is a tremen-

dous task, but the result will prove worthy of the effort and constitute an everlasting memorial to the ideals of Edward Orton, Jr.

Acknowledgment

In closing I should like to express my sincerest thanks to all from whose published data I have freely drawn in compiling this paper, thereby broadening its scope far beyond my own contributions to this field. Specifically, I should like to mention W. Bilke, W. H. and W. L. Bragg, S. M. Brown, W. H. Dore, K. Endell, W. F. Foshay, J. E. Gieseking, R. E. Grim, J. W. Gruner, S. B. Hendricks, U. Hofmann, R. Houwink, H. Jenny, W. P. Kelley, P. F. Kerr, E. Maegdefrau, C. E. Marshall, Sante Mattson, G. Nagelschmidt, W. Noll, F. H. Norton, P. G. Nutting, L. Pauling, C. S. Ross, B. E. Warren, and G. Wiegner

The complete models illustrating the structure of alkali silicates and clay minerals as well as those that were built during the presentation of this lecture were made by a simple and inexpensive method, details of which appeared in the *Journal of Chemical Education*, **18** [4] 164 (1941).

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FUNDAMENTAL STUDY OF CLAY: II, MECHANISM OF DEFLOCCULATION IN THE CLAY–WATER SYSTEM*

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Abstract

The effect of bases, basic salts, neutral salts, acid salts, and acids on the viscosity of clay slips cleaned as described in Part I of this study is shown. From these data, a fundamental theory of deflocculation is built up, based on the fact that deflocculation requires the presence of OH anions and monovalent cations. The influence on the viscosity of small traces of soluble salts or adsorbed ions, which are present in commercial clays, is discussed. It is also shown why sodium silicate or carbonate works more satisfactorily than sodium hydroxide in the deflocculation of commercial casting slips.

I. Introduction

The purpose of this paper is to present a theory for the mechanism of deflocculation by means of a study of the effect of electrolytes on the viscosity of dilute suspensions of clean kaolinite. The study does not include the protective action of lyocratic colloids, such as gums, etc., which is not influenced by the presence of electrolytes. Using clean kaolinite (prepared as described in Part I[1]), the effect of electrolytes, such as bases, salts, and acids, on the viscosity of the suspension may be readily determined. The use of clean clay eliminates uncertainties caused by the presence of soluble salts or other material and in general facilitates the interpretation of the results, which are always reproducible inasmuch as the system is well defined. With a better knowledge of the deflocculation process as it occurs with clean kaolinite, the effect of soluble salts or other deliberately added substances may be systematically studied.

(1) Historical

As Hauser[2] puts it, there was no need to discover colloids because their existence was known and many of their properties were recognized centuries ago. Burton,[3] Auscher,[4] and Brongniart,[5] who trace the historical development of porcelain manufacture in England, France, and Germany, state that "casting" in plaster molds originated between the years 1700 and 1740. The "casting slips" of that period were low specific gravity mixtures of clay and water which were so viscous they had to be scooped into the plaster molds. The process required much time, and the resulting cast was uneven and extremely flabby because no deflocculants were used.

It is difficult to state with any degree of accuracy exactly when the action of alkalis or basic salts on clay pastes was known. This action, however, undoubtedly was studied by many long before its commercial application was revealed. Brongniart[5] tells of a M. de Bettignies who, in 1844, used 3% of potassium carbonate with his "casting pastes" to give a necessary "adherence" to the mold. This "adherence" probably refers to a firmer cast that would result from the use of deflocculated slips.

The first public announcement concerning the use of electrolytes with clay pastes for the precise purpose of increasing the fluidity of the slip must therefore be attributed to Goetz,[6] who applied for a patent in Germany on October 22, 1891. A portion of the translated patent reads as follows:

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 1, 1941 (White Wares Division). Received March 3, 1941.

[1] A. L. Johnson and F. H. Norton, "Fundamental Study of Clay: Preparation of a Purified Kaolinite Suspension, I," *Jour. Amer. Ceram. Soc.*, **24** [2] 64–69 (1941).

[2] E. A. Hauser, Colloidal Phenomena. McGraw-Hill Book Co., Inc., New York, 1939; *Ceram. Abs.*, **18** [10] 283 (1939).

[3] W. Burton, Porcelain, Its Art and Manufacture. B. T. Bradford, Ltd., London, 1906.

[4] E. S. Auscher, History of French Porcelain. Cassell & Co., New York, 1905.

[5] A. Brongniart, Traité des Arts Céramique, Vol. II, p. 469. Béchet Jeune, Paris, 1854.

[6] C. Goetz, German Pat. 76,247 (1891).

Preparation of casting slips for porcelain, earthenware, and clay products by the addition of sodium carbonate or bicarbonate, with or without cinabar, whereby the slip will pour more readily.

After this patent was granted in 1894, other patents[7] followed on the use of various electrolytes as deflocculants, such as water glass. Weber[8] was granted a patent for the manufacture of articles made from fire-clay-grog mixtures by the casting process in Germany during 1903. Thus, soon after the beginning of the 20th century, the use of deflocculants in the preparation of casting slips, substantially as they are known today, was common knowledge.

(2) Theories

Technical papers on the casting process began to make their appearance after 1900. Weber[9] attempted to explain the reason why certain plastic clays could not be "liquefied" by the addition of small quantities of alkali and showed that interfering soluble salts, specifically the sulfate radicle, hindered the reaction. Basing his reasoning on the Schloesing[10] theory of plasticity propounded some thirty years earlier, Weber reasoned that the sulfate ion precipitated the colloidal element of the clay thereby preventing the "liquefaction" of the clay by the alkali unless the interfering material was first neutralized. This rather simple explanation of the colloidal nature of clay introduced questions which needed to be answered before there could be a better understanding of the deflocculation process. The deflocculation of clays generally has been assumed to be accomplished by charging the "colloidal" material of the clay. The charged particles repel each other, and there is a simultaneous release of the "bound" water. The combined effect of the charging of the particles and the release of the bound water is said to cause the fluidity[11] of a slip to increase.

The physical interpretation of the development of the charge on colloidal particles today is based on the Gouy-Freundlich[12] concept of the diffuse double layer. The formation of this double layer, according to Hauser,[2] can be arrived at either by (*a*) the preferential adsorption of ions or (*b*) the surface dissociation of ions. Neither phenomenon will be discussed in detail, but, for clarity, some of the theories put forth by investigators will be classified into one or the other group.

(*A*) *Development of Charge by Preferential Adsorption:* In 1910, Spangenberg[13] claimed that the clay colloid adsorbed (OH) ions and in this manner became negatively charged. The (clay-OH) particles then repel each other electrostatically. Bleininger,[14] Mattson,[15] Freundlich,[12(b)] Weber,[9] Kondo,[16] Wettig,[17] Comber,[18] Ashley,[19] and Henry and Taylor[20] also believed that the formation of this (clay-OH) complex was the reason for the development of the charge. Because the development of the charge on the clay particle depended on the adsorption of (OH) ions by the particle, it follows that deflocculation of slips should be brought about by the addition of alkalis to the clay–water system. This, however, is not always the case, and reasons for the failure of alkalis to produce the best results are divided into two lines of thought.

(i) *Theory of First Group:* The first group holds to the theory (with Weber[9]) that the presence of soluble salts causes the precipitation of the clay colloid and thereby prevents the action of the alkali. Certain salts could be used because their action is first to neutralize the effect of the interfering soluble salt. Mattson[15] strongly believes in the adsorption of the hydroxyl ions and the resulting dispersion of the clay owing to the increased charge even in the presence of relatively strong cations. The role of the cations, he believes, is that of positive hydrated particles interspaced among the negatively charged clay particles. Kondo[16] makes important observations as follows:

(1) NaOH is not detectable in suspensions of pure clay unless added in excess; (2) hydrogen ions are likewise not detectable unless acid is added; and (3) salts which do not hydrolyze cause coagulation.

In summarizing the work of others, Kondo[16] proposes the following theory on the action of alkalis on clays:

$$HA + KOH \longrightarrow KA + H_2O$$
$$KA \rightleftharpoons K^+ + A^-$$

Where A = kaolinite acid radicle or its fraction.

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[7] (*a*) A. Schmidt, *Sprechsaal*, **27**, 664–89 (1894); (*b*) K. Greiner, *Halle*, **54** (1903); and (*c*) A. Johnson, British Pat. 14,908 (1905).

[8] E. Weber, German Pat. 159,496 (1903).

[9] E. Weber, "Liquefaction of Clays by Alkalis and Use of Fluid Clay Casting in Ceramic Industry" (translation), *Trans. Ceram. Soc.* [England], **8**, 11–22 (1908–1909).

[10] (*a*) T. Schloesing, "Constitution of Clays," *Compt. rend.*, **78**, 1438–42 (1874); (*b*) Second and Third Notes, *ibid.*, **79**, 376–80 and 473–77 (1874).

[11] (*a*) J. van Bemmelen, *Die Absorption* (1910).

(*b*) R. A. Gortner, "Water in Living and Colloidal Systems," *Trans. Faraday Soc.*, **26**, 678 (1930).

(*c*) D. R. Briggs, "Water Relationships in Colloids, II," *Jour. Phys. Chem.*, **36** [1] 367–86 (1932); *Ceram. Abs.*, **11** [5] 330 (1932).

[12] (*a*) M. Gouy, "Sur la Constitution de la Charge Electrique a la Surface d'un Electrolyte," *Jour. phys.* [4th Series], **9**, 457–68 (1910).

(*b*) H. Freundlich, Kapillarchemie, Vol. 1, 4th ed., p. 356. Akad. Verlags.-Ges., Leipzig, 1930.

[13] A. Spangenberg, Zin Erkenntnis des Tongreszen ihren Einflusz auf die Tonverflüssigung. Dissertation, Darmstadt, 1910.

[14] A. V. Bleininger, "Use of Sodium Salts in Purification of Clays and in the Casting Process," *Nat. Bur. Stand. Tech. Paper*, No. 51, p. 7 (September 25, 1915).

[15] S. E. Mattson, "Beziehungen zwischen Ausflockung, Adsorption, und Teilchenladung mit besonderer Berücksightgung der Hydroxyleionen," *Kolloidchem. Beihefte*, **14** [9–12] 227–331 (1921–1922).

[16] S. Kondo, "Action of Electrolytes on Clays, III," *Jour. Soc. Chem. Ind.* [Japan], **323**, 1–10 (1925); *Ceram. Abs.*, **5** [1] 33 (1926).

[17] E. Wettig, "Casting Slip Problem in Light of Recent Research Work," *Ber. deut. keram. Ges.*, **17** [3] 137–49 (1936); *Ceram. Abs.*, **15** [10] 306 (1936).

[18] N. F. Comber, "Role of Electronegative Ions in Reactions Between Soils and Electrolytes," *Trans. Faraday Soc.*, **20**, 567 (1924).

[19] H. E. Ashley, "Technical Control of Colloid Matter in Clays," *Trans. Amer. Ceram. Soc.*, **12**, 768–817 (1910).

[20] E. C. Henry and N. W. Taylor, "Acid and Base Binding Capacities and Viscosity Relations in Certain Whiteware Clays," *Jour. Amer. Ceram. Soc.*, **21** [5] 165–75 (1938).

The Wettig[17] picture of the clay molecule is one consisting of a negatively charged acid residue whose lattice structure exhibits a residual negative charge at the surface and corners. The most important seats of these charges occur at the corners and edges so that, although water molecules may be adsorbed at the surfaces, ionic reactions and salt formation can take place at these highly charged centers. The strength of the electric fields at these "störungsstellen" is not great enough to neutralize completely the full charge of the positive ions such as Na^+ or K^+ so that these satisfy their charges by the adsorption of water molecules.

(ii) *Theory of Second Group:* The second group holds to the belief that the cation introduced with the (OH) radicle has a flocculating effect on the colloid. According to McDowell,[21] the effect of the cation must therefore be neutralized. The mechanism of this process is to introduce a salt which hydrolyzes to yield (OH) ions in solution, thus supplying the clay particle with the necessary ions in order to build up a negative charge. The effect of the cation is neutralized by a protective action of the colloidal silica, for example, that formed upon the hydrolysis[22] of sodium silicate. Bole[23] assumes that the clay has an original negative charge and thus is able to adsorb a coating of positively charged colloidal material of unknown composition. The addition of sodium hydroxide then causes the formation of a "hydroxyl ion-colloid complex" which results in the deflocculation of the system. According to the Freundlich[24] preferential adsorption theory, Bole believes that the hydroxyl ions may be adsorbed more readily than the sodium ions at low concentrations, whereas the reverse may hold true at higher concentrations of sodium hydroxide. This would explain the gelation of the slips at higher concentrations of electrolyte. Webb[25] states that certain organic materials can also exert this protective action. Neubert[26] claims that humus does more than exert a protective action on the system, whereas Webb[25] disagrees and says that any role other than one of protection by the organic matter is unnecessary and unconfirmed. Hall,[27] Keppeler,[28] Snell,[29] Williamson,[30] Neuss,[31] and King[32] agree with this protective theory. Dyachkov[33] has shown that sodium-aluminate solutions will deflocculate clays with a protective action similar to that of sodium silicate, that is, a layer of colloidal Al_2O_3 surrounds the clay particle.

(*B*) *Development of Charge by Surface Dissociation:* Lewis, Squires, and Thompson[34] believe in the surface dissociation theory and claim that although the hydroxyl group of the clay lattice is amphoteric it is also mainly acidic in character. These groups are highly polar and exert a strong attraction force between particles causing the formation of "flocs." Metal salts are capable of replacing the hydrogen in the OH group, and, because of the dissociation of the former, increased repulsion forces between particles are set up which result in the lower viscosity and yield value of clay suspensions to which these metal ions have been added. Bradfield,[35] Michaelis,[36] and Kelley and Jenny[37] also advocate this theory. Houwink[38] agrees in part with this idea, but he adds that the cations situated between the layers in the lattice structure are of no particular use in a study of the nature of the electrical forces between particles. Hofmann and Bilke[39] believe that cations are directly adsorbed onto the clay particle because of the unsaturated condition of oxygen atoms in the Si–O tetrahedra along the edges (shown in Fig. 1); this was a new concept, but it may be classified in this category.

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[21] S. J. McDowell, "Effect of Various Sodium Silicates and Other Electrolytes on Clay Slips," *Jour. Amer. Ceram. Soc.*, **10** [4] 225–37 (1927).

[22] (*a*) F. Koherausch, "Über Lösungen von Natrium-Silicaten," *Z. physik. Chem.*, **12**, 773 (1893).
(*b*) E. Jordis, "Über die Darstellung krystallisierter Natriumsilicate," *Z. angew. Chem.*, **20**, 1410 (1907).
(*c*) L. Wasilewski and W. Badzynski, "Measurement of Velocity of Hydrolysis of Aqueous Solutions of Water Glasses," *Przemysl Chem.*, **15**, 185–88 (1931); *Ceram. Abs.*, **11** [4] 279 (1932).
(*d*) R. W. Harman, "Aqueous Solutions of Sodium Silicates," *Jour. Phys. Chem.*, **31** [3] 355–73 (1927); *Ceram. Abs.*, **6** [5] 189 (1927).

[23] G. A. Bole, "Mechanism of Plasticity from a Colloid Standpoint," *Jour. Amer. Ceram. Soc.*, **5** [8] 469–77 (1922).

[24] H. Freundlich, Kapillarchemie, p. 351. Leipzig, 1909.

[25] H. W. Webb, "Alkaline Casting Slip, I," *Trans. Ceram. Soc.* [England], **33**, 129–67 (1934); *Ceram. Abs.*, **17** [4] 146 (1938).

[26] J. V. Neubert, "Die Tonverflüssigung durch Alkali," *Kolloidchem. Beihefte*, **4**, 261 (1912).

[27] F. P. Hall, "Casting of Clayware, A Résumé," *Jour. Amer. Ceram. Soc.*, **13** [10] 751–66 (1930).

[28] Gustav Keppeler, "Untersuchungen über den grünen Zustand des Tones," *Ber. deut. keram. Ges.*, **3**, 257–70 (1922); *Ceram. Abs.*, **5** [2] 67 (1926).

[29] F. D. Snell, "Detergency of Alkaline Salt Solutions, III," *Ind. Eng. Chem.*, **25**, 162 (1933).

[30] (*a*) W. T. H. Williamson, "Advances in Chemistry of Soils," *Chemistry & Industry*, **47**, 391 (1928); *Ceram. Abs.*, **7** [7] 491 (1928).
(*b*) W. T. H. Williamson, "Suspensions and Their Relation to Colloid Stability," *Jour. Soc. Chem. Ind.*, **44**, 402 (1925); *Ceram. Abs.*, **4** [7] 203 (1925).

[31] O. Neuss, "Flowability of Fat, Highly Refractory Clays," *Feuerfest*, **3** [7] 109–11 (1927); *Ceram. Abs.*, **6** [11] 528 (1927).

[32] R. M. King, "Lignin Extract as Bonding Agent for Ceramic Bodies," *Ceram. Ind.*, **14** [1] 62–64 (1930); *Ceram. Abs.*, **9** [5] 389 (1930).

[33] V. D. Dyachkov, "Interaction of Sodium Aluminate and Silicate Solutions," *Zhur. Priklad. Khim.*, **10**, 1211–15 (1937); *Ceram. Abs.*, **17** [4] 162 (1938).

[34] W. K. Lewis, Lombard Squires, and W. I. Thompson, "Colloidal Properties of Clay Suspensions," *Trans. Amer. Inst. Mining Met. Engrs.*, **114**, 38–52 (1935); *Ceram. Abs.*, **17** [3] 115 (1938).

[35] R. Bradfield, "Nature of Acidity of the Colloidal Clay Solid," *Jour. Amer. Chem. Soc.*, **45**, 2669 (1923).

[36] Leonar Michaelis, "General Principles of Ion Effects on Colloids," *2nd Colloid Symposium Monograph, Northwestern Univ.*, 1924 (published 1925); *Ceram. Abs.*, **4** [12] 360 (1925).

[37] W. P. Kelley and Hans Jenny, "Relation of Crystal Structure to Base Exchange and Its Bearing on Base Exchange in Soils," *Soil Sci.*, **41**, 367–82 (1936); *Ceram. Abs.*, **19** [5] 124 (1940).

[38] R. Houwink, Elasticity, Plasticity, and Structure of Matter. University Press, Cambridge, England, 1937; *Ceram. Abs.*, **17** [6] 235 (1938).

[39] U. Hofmann and W. Bilke, "Über die Innerkristalline Quellung und das Basenaustaus chvermögen des Montmorillonits," *Kolloid-Z.*, **77**, 238–51 (1936).

Several miscellaneous theories have been put forth and are worthy of comment. Fodor and Schoenfeld[40] and Kohl,[41] who use the Perrin and Duclaux[42] concept of the micelle, believe that both the hydrogen and hydroxyl ions of the water molecule are adsorbed by the clay particle but that, owing to the character of the clay, all of the hydroxyl ions are not neutralized, which leaves the clay with a net negative charge.

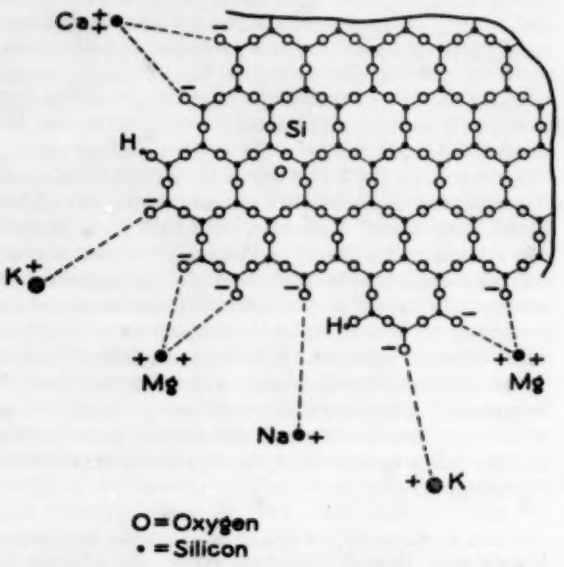

FIG. 1.—Unsaturated oxygen atoms in Si–O tetrahedra showing equilibrium distance of cations redrawn according to Hofmann and Bilke.[39]

The majority of these theories deal with the mechanism of deflocculation as it is brought about by the addition of a specific electrolyte. Certain investigators recently have taken a broader view, and they attempt to explain the stability of electrocratic systems as it is affected by electrolytes in general. These theories are based on the work of London[43] and of Kallmann and Willstaetter,[44] who have theorized that the van der Waals forces are additive and therefore can act over distances greater than those of monomolecular proportions. On this basis, it is claimed that attraction forces (van der Waals forces) and repulsion forces resulting from the charge on the particles play an important part in controlling the stability of the system.

Freundlich,[45] in collaboration with Rubin, must be credited with a graphical description by which the nature of these attraction-repulsion forces may be visualized. Figure 2 represents a plot of these forces established between particles as a function of the distance of separation for various concentrations of electrolyte.

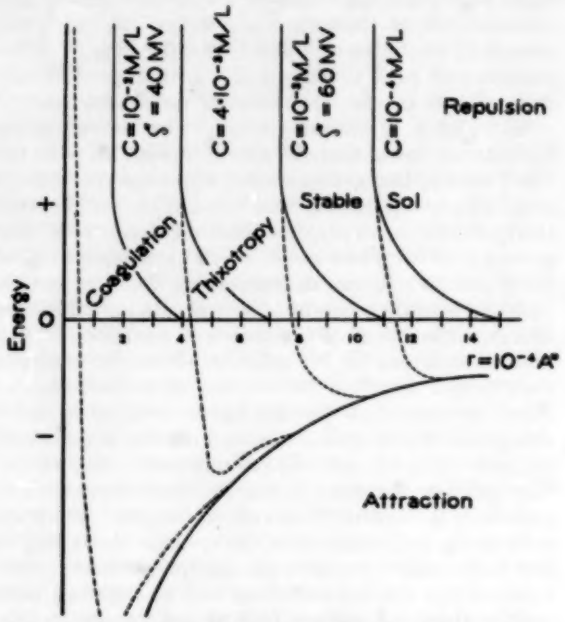

FIG. 2.—Energy potential curves redrawn from data according to Freundlich.[46]

The dotted lines represent the summation of the attraction-repulsion forces; this shows that if the repulsion between particles is stronger at small separations there will be a potential "trough" or minimum at greater separations (because the repulsion forces approach zero more rapidly than the attraction forces).

Hamaker[46] has reported recently a more detailed study of the van der Waals-London theory and its application to the stability of colloidal systems by means of a potential curve (Fig. 3). The application of the potential curves is discussed in some detail by Hauser (p. 219)[2] and Houwink (p. 341).[38] Houwink admits that certain effects, such as the decrease in viscosity and that of neutral electrolytes (NaCl), are not easily explained, but he attributes this to a lack of suitable data and advocates a more thorough investigation.

From a colloidal standpoint, Hauser (p. 223)[2] raises certain objections to this viewpoint because it fails to take into consideration the entire colloidal micelle and the dispersion medium. Ostwald[47] believes that the stability of an electrocratic system depends on the

[40] A. Fodor and B. Schoenfeld, "Beitrage zur Kenntnis der Kolloidnatur der Tone," *Kolloidchem. Beihefte*, **19**, 1–46 (1924); *Ceram. Abs.*, **3** [8] 252 (1924).

[41] H. Kohl, Kolloidchemie in der Keramik. Theodor Steinkopff, Dresden and Leipzig, 1931; *Ceram. Abs.*, **10** [12] 870 (1931).

[42] J. Duclaux, "Die Filtration kolloid Losüngen," *Kolloid-Z.*, **3**, 126 (1908).

[43] H. Kallmann and F. London, "Über quantenmechanische Energieübertragung zwischen atomen Systeme," *Z. physik. Chem.*, **B2**, 207 (1929).

[44] H. Kallmann and M. Willstaetter, "Zur Theorie des Aufbaues kolloidaler Systeme," *Naturwissenschaften*, **20**, 952 (1932).

[45] H. Freundlich, Thixotropy. Herman & Cie, Paris, 1935.

[46] H. C. Hamaker, "General Theory of Lyophobic Colloids," *Rec. trav. chim.*, **55**, 1015–26 (1936).

[47] W. Ostwald, "Electrolyte Coagulation and Coefficient of Electrolyte Activity," *Jour. Phys. Chem.*, **42**, 981 (1938).

dispersion medium, and Hardy[48] has shown the importance of the charge on the particle in relation to the stability of the system.

It must be considered as a distinct contribution, therefore, when Hauser and Hirshon[49] presented a theory explaining the stability of electrocratic systems on the basis of electrical or coulombic forces only. This theory differs from the foregoing ideas in that it deals with the *ions* of the entire system, which include those in the dispersion medium. Their idea of "condensation and orientation" of the charges will be discussed in a later section.

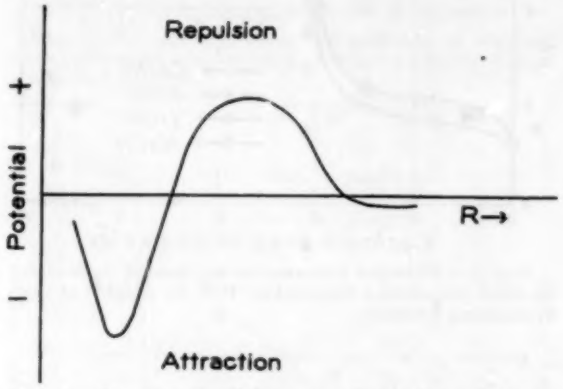

FIG. 3.—Energy-potential curve redrawn from data according to Hamaker.[46]

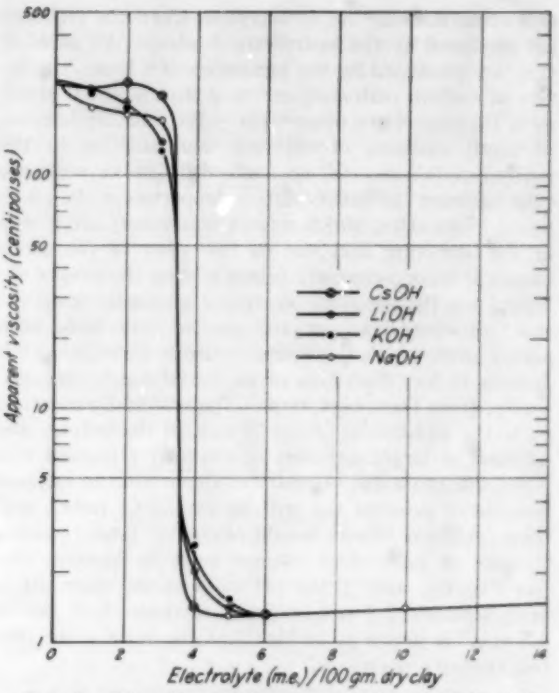

FIG. 4.—Viscosity relations on addition of hydroxides of alkali metals to a suspension (16% by weight) of electrodialyzed kaolinite.

II. Experimental Data on Clean Kaolinite Slips

A great deal of material has been published on deflocculation of clay slips and has been mentioned in the references. In no case, however, was the clay slip thoroughly cleaned of the disturbing impurities, such as soluble salts, organic matter, and adsorbed ions which so profoundly influence the results, as will be shown later. Most of the previous data for this reason have been unsuitable for a careful study of the mechanism of deflocculation. It has been found necessary in this study to work only with clay slips which have been cleaned as thoroughly as possible to eliminate the influence of unwanted ions and to give sharp and definite breaks in the viscosity curve.

(1) Procedure

The measurement of viscosity and pH of clean Florida kaolin, made up to a specific gravity of 1.10 corresponding to 16% of solids by weight, was determined by the method described in Part I.[1] By the use of the modified McMichael viscosimeter, the viscosity readings are precise even at low viscosities.

(2) Results

To define more clearly the mechanism of deflocculation so that the various theories may be tested, a number of typical electrolytes were added in varying amounts to make up the 16% suspension of clean Florida kaolin, and values of viscosity and pH were measured.

The various electrolytes may be logically classified into five divisions which, with the actual electrolytes used, are indicated in Table I. Although the number of electrolytes used is not entirely comprehensive, it is sufficiently widespread to bring out the pertinent facts. Calcium and magnesium hydroxides could not be used because of their insolubility.

TABLE I

Series No.	Electrolyte: Type	Electrolyte: Actually tried	Results shown in figs.
1	Bases	CsOH, LiOH, KOH, NaOH, $Sr(OH)_2$, $Ba(OH)_2$	4–7
2	Basic salts*	Na_2CO_3, Na_2SiO_3, $(NH_4)_2C_2O_4$	8–9
3	Neutral salts	NaCl, Na_2SO_4	10–11
4	Acid salts†	NH_4Cl	10–11
5	Acids	HCl, $H_2C_2O_4$	10–11

* Basic salts hydrolyze to give $(OH)^-$.
† Acid salts hydrolyze to give $(H)^+$.

If the minimum viscosity is assumed to be a criterion of the deflocculation effect of the electrolyte, the results may be clearly summarized as shown in Table II. The following conclusions may therefore be derived: (*a*) deflocculation occurs only when OH ions are present in the suspending medium; (*b*) complete deflocculation takes place only when the cation is monovalent; (*c*)

[48] W. B. Hardy, "Über den Mechanismus der Erstarrung in umkehrbaren Kolloidsystemen," *Z. physik. Chem.*, **33**, 326 (1900).
[49] E. A. Hauser and S. Hirshon, "Behavior of Colloidal Suspensions with Electrolytes," *Jour. Phys. Chem.*, **43**, 1015–36 (1939); *Ceram. Abs.*, **19** [6] 146 (1940).

deflocculation may be as complete when the OH ions are produced by the hydrolysis of a basic salt as when they are produced by the ionization of a base; the action of sodium carbonate on these slips is not as sharp as in the case of the other basic salts, possibly because of small amounts of chlorides and sulfates in the sodium carbonate; (*d*) no marked difference seems to exist between the deflocculating properties of the alkali metal hydroxides, which refutes statements often seen in the literature that one or the other of the alkali metals is more powerful; (*e*) on adding the proper deflocculant, the viscosity decreases gradually until 3.5 m.e.* of electrolyte per 100 gm. of clay have been added, after which the viscosity drops with great suddenness to less than $^1/_{100}$ of its initial value; the viscosity, from this point, remains substantially constant up to the addition of about 20 m.e. of electrolyte; the addition of larger amounts of electrolyte beyond this point will cause the viscosity of the system to increase because of gelation (as will be explained later), and these gelation effects would occur at lower concentrations of polyvalent cations such as barium, etc. (see Fig. 6); and (*f*) the pH value of the clean slip is approximately 5.3 and gradually increases to 6, but at 3.5 m.e.* it jumps up suddenly at the same point that the viscosity decreases.

TABLE II

MINIMUM VISCOSITY IN CENTIPOISES

	Anions					
Cations	OH	CO_3	SiO_3	C_2O_4	SO_4	Cl
Cs	1.3					
Li	1.3					
K	1.3					
Na	1.3	1.7	1.7		80	140
NH_4				2.0		
Ba	70					
Sr	90					
H	250			150		170

III. Mechanism of Deflocculation in Clean Clay Suspension

The foregoing discussion of the experimental results has shown the type and amount of electrolyte needed to deflocculate clean electrodialyzed kaolinite slips. An explanation of this phenomenon is now attempted on the basis of these results.

(1) Formation of Diffuse Double Layer

Before an accurate picture of the clay particle and its charge can be obtained, the reason for the formation of the double layer must be determined. The two basic methods by which this double layer can form, as mentioned by Hauser,[2] are the preferential adsorption method or the surface dissociation of ions. No definite information is yet available, relating to the clay systems, as to whether or not the formation of the double layer is brought about by either one or the other method. Because, however, of certain similarities to systems whose charge has been traced to the preferential adsorption of ions, this mechanism is in favor at the present time. The discussion of the charge on the clay particle consequently will be based on the development of that

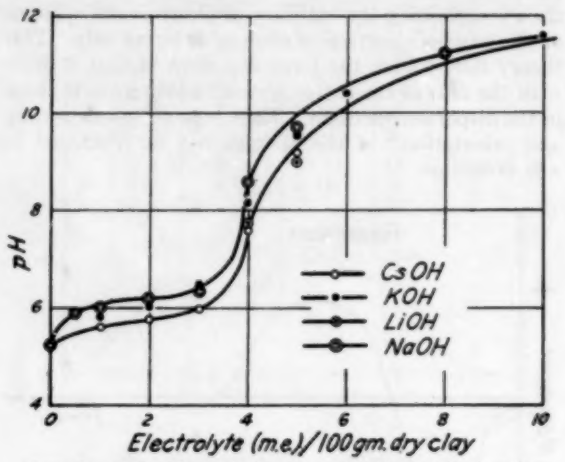

FIG. 5.—Titration relations on addition of hydroxides of alkali metals to a suspension (16% by weight) of electrodialyzed kaolinite.

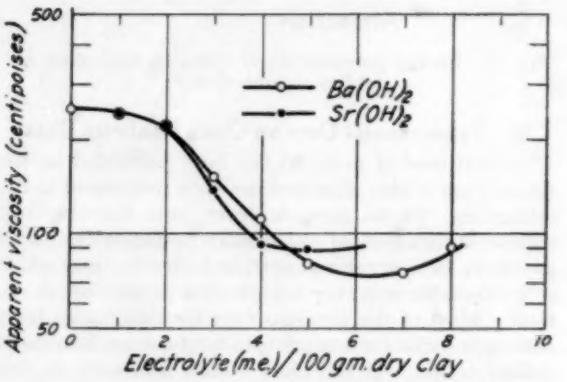

FIG. 6.—Viscosity relations on addition of alkaline earth hydroxides to a suspension (16% by weight) of electrodialyzed kaolinite.

charge as a result of the preferential adsorption of certain ions. Several points to be mentioned later will indicate that this is probably the correct interpretation.

Langmuir[50] has shown that the preferential adsorption of ions by substances is the result of the presence of active areas on the surface of the crystal. Schofield[51] believes that positive and negative areas exist on clay crystals, which may be accounted for on the basis of the atomic structure as revealed by X-ray analysis; the presence of these areas explain the "retention" of anions

* The break in the viscosity and titration curves were first shown to occur at 4.5 m.e. of electrolyte (see Part I[1]); the change to 3.5 m.e. is the result of the more careful cleaning treatment afforded the latter samples.

[50] (*a*) Irving Langmuir, "Constitution and Fundamental Properties of Solids and Liquids: I, Solids," *Jour. Amer. Chem. Soc.*, **38**, 2221–95 (1916); (*b*) "Adsorption of Gases on Plane Surfaces of Glass, Mica, and Platinum," *ibid.*, **40**, 1361 (1918).

[51] R. K. Schofield, "Clay-Mineral Structures and Their Physical Significance," *Trans. Ceram. Soc.* [England], **39** [5] 147–61 (1940); *Ceram. Abs.*, **20** [1] 27 (1941).

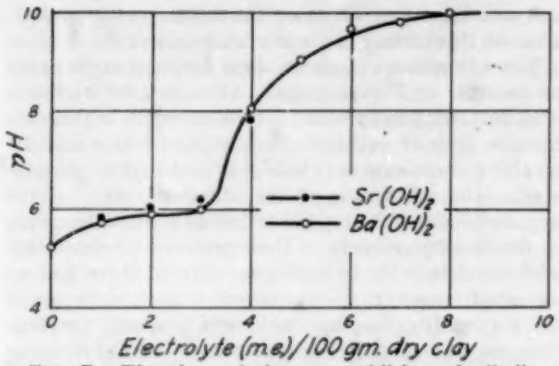

FIG. 7.—Titration relations on addition of alkaline earth hydroxides to a suspension (16% by weight) of electrodialyzed kaolinite.

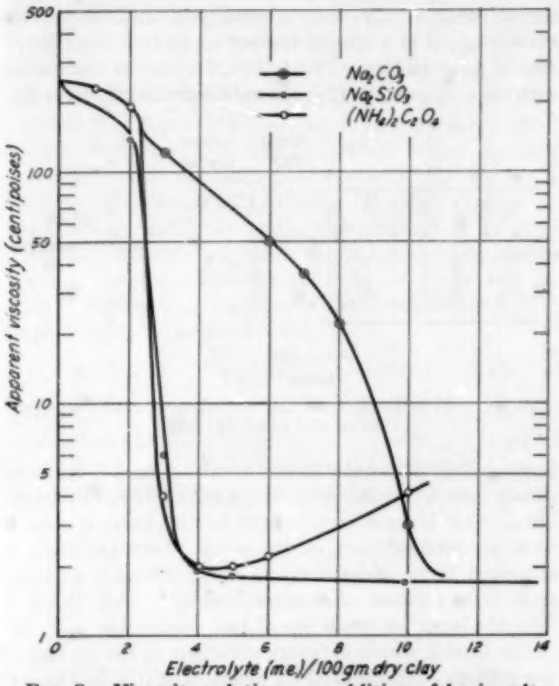

FIG. 8.—Viscosity relations on addition of basic salts to a suspension (16% by weight) of electrodialyzed kaolinite.

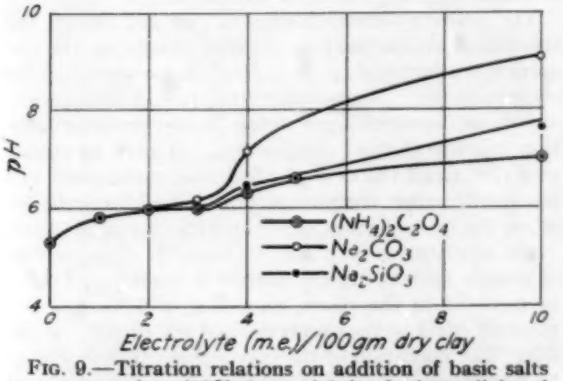

FIG. 9.—Titration relations on addition of basic salts to a suspension (16% by weight) of electrodialyzed kaolinite.

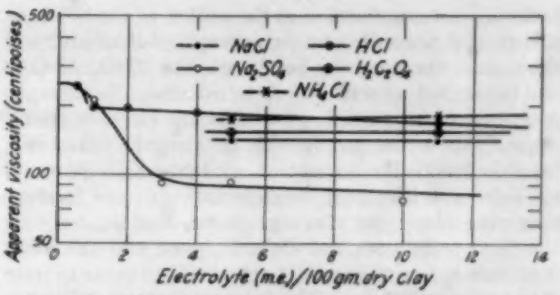

FIG. 10.—Viscosity relations on addition of neutral salts, acid salts, and acids to a suspension (16% by weight) of electrodialyzed kaolinite.

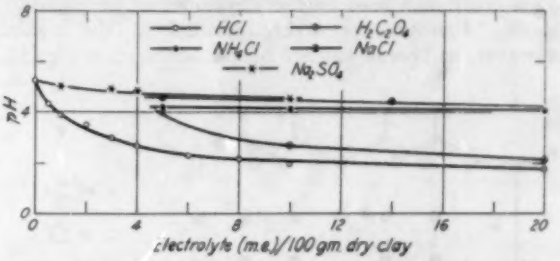

FIG. 11.—Titration relations on addition of neutral salts, acid salts, and acids to a suspension (16% by weight) of electrodialyzed kaolinite.

and cations in "equivalent amounts"; furthermore, the degree of "retention" depends on the type and amount of ions in the system. Ford, Loomis, and Fidiam[52] attempt to show how the adsorption of certain chemicals on specific parts of the crystal faces of clay particles can reduce the viscosity of a clay suspension by a breakdown of the aggregation of particles.

Grim[53] believes that, among some clay minerals, a replacement of certain atoms of the crystal lattice by metals of lower valency will cause the formation of charged areas; in a comprehensive study of these replacements, he shows how the substitution of the Al^{+++} positions by Mg^{++} in the gibbsite layer or of the Si^{++++} by Al^{+++} in the silica tetrahedral sheets (for example, in the montmorillonite structure) can produce a negative charge on certain areas of the crystal. The particle therefore obtains a net negative charge without the adsorption of anions and is capable of attracting cations, which explains the base-exchange capacity of this mineral; according to Grim,[53] no replacements of this type in kaolinite have been proved, and, in any event, this would not explain the formation of a charged area in pure kaolinite [$Al_2Si_2O_5(OH)_4$] where no replacement exists. The development of the "active" areas in kaolinite therefore needs more careful consideration.

The kaolinite crystal is built up of silicon and aluminum layers (see Fig. 12). The crystal displays perfect basal cleavage, and along this cleavage plane no unsaturation can result from fracture, that is, no bonds are

[52] T. F. Ford, A. G. Loomis, and J. F. Fidiam, "Colloidal Behavior of Clays as Related to Their Crystal Structure," *Jour. Phys. Chem.*, **44**, 1–12 (1940); *Ceram. Abs.*, **19** [6] 146 (1940).

[53] R. E. Grim, "Relation of Composition to the Properties of Clays," *Jour. Amer. Ceram. Soc.*, **22** [5] 141–51 (1939).

broken. An examination of the nature of the bonds in this crystal, according to the concepts of Pauling,[54] will show that the weakest bonds are the Al–O, Al–OH, and the shared corners of Si–O tetrahedra. Photographs of fine kaolinite particles, taken by the electron microscope,[55] show the particle to be roughly hexagonal; on this basis, the formation of hexagonal plates of kaolinite particles may be expected with one fracture occurring along the cleavage plane, that is, between the Si–O tetrahedra and the OH layer, and the other fractures occurring parallel to the *c*-axis in order to form thin hexagonal plates. The fracture along the cleavage plane thus causes no valence bonds to be broken and therefore no unsaturation of valence should result. This could not lead to the development of "active" spots. Fractures occurring parallel to the *c*-axis, however, will break valence bonds, as shown in Fig. 13,

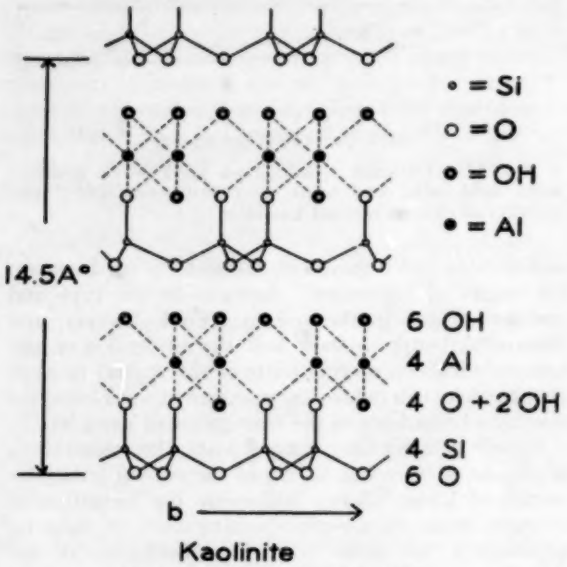

FIG. 12.—Structure of kaolinite.

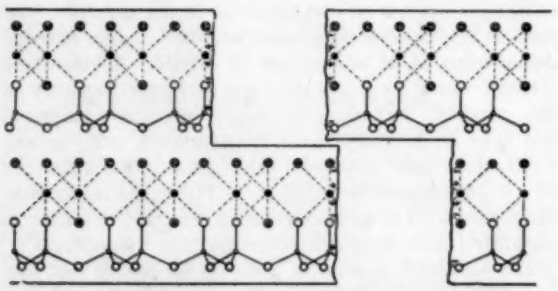

FIG. 13.—Fractured crystal of kaolinite showing unsaturated areas due to broken valence bonds.

and such fractures will cause the formation of "active" areas on this surface of the crystal fragment.

The adsorption of ions on these active spots is based on the rule of Fajans-Hahn. Aluminum or hydroxyl ions, according to this law, can be adsorbed in this case because they fit well into the kaolinite lattice and the resulting combination is insoluble and slightly dissociated. The adsorption of the aluminum ions on the negative zones of the crystal fragment is unlikely, owing to the small possibility of their presence in connection with the formation of kaolinite. Should these ions be adsorbed, however, the dispersion of such clays would not be readily accomplished, which would preclude their use immediately because of their state of flocculation. The effect of the aluminum ion on clays will be discussed later.

The adsorption of the hydroxyl ion by the positive active areas is the only alternative, and, with this knowledge, it is a simple matter to picture the diffuse double layer of Gouy-Freundlich,[12] which is associated with the clay particle (Fig. 14 shows such a clay micelle).

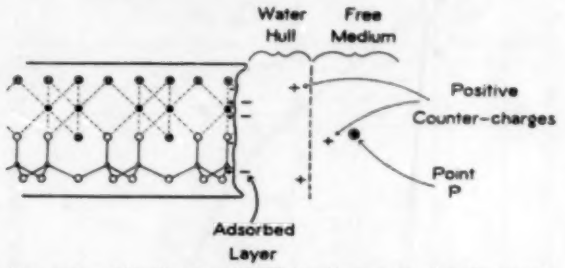

FIG. 14.—Micelle of a kaolinite fragment showing position of adsorbed cations.

Immediately adjacent to the specified active areas on the surface of the clay particle are the adsorbed hydroxyl ions. This layer is firmly held by the particle as if it were an integral part of the solid. Surrounding this adsorbed layer and extending a considerable distance from it is a cloud of countercharges. This cloud or "double layer" is made up of two parts; the first, lies in the liquid, which is firmly attached to the surface of the particle (represented by the dotted line in Fig. 14) and the second is located in the free medium and extends into the medium up to point *P*, where the mean electric charge approaches a zero value.

The positive countercharges can be any cation, but the charge on the particle depends chiefly on the dispersion medium and on the type of cation serving as the countercharge. Natural clays may have a wide variety of ions as countercharges owing to the possible variation in mineralogical composition. It may be readily seen that small traces of a substituted montmorillonite can greatly alter the picture of a colloidal micelle because the montmorillonite obtains its charge by virtue of the substitution (as shown by Grim[53]). The presence of soluble salts or organic matter in commercial clays, as received in the plant, moreover, will have a pronounced effect on the properties and stability of the clay slip. The condition of the clay system therefore must be accurately defined before reports on the properties of the systems can be correctly analyzed.

[54] Linus Pauling, Nature of Chemical Bond and Structure of Molecules and Crystals. Cornell University Press, Ithaca, N. Y., 1940; *Ceram. Abs.*, **19** [1] 28 (1940).

[55] W. Eitel, H. O. Müller, and O. E. Radczewski, "Ultramicroscopic Examination of Clay Minerals," *Ber. deut. keram. Ges.*, **20** [4] 165–80 (1939); *Ceram. Abs.*, **18** [8] 222 (1939).

With special emphasis thus placed on the selection and treatment of this sample of kaolinite, the slip, after electrodialysis, may be represented in the simplified form shown in Fig. 15. Immediately adjacent to the active areas is situated the adsorbed OH layer. Although the cloud of countercharges exists as before, the cation in this case is the hydrogen ion. The kaolinite micelle is surrounded by a pure water medium. The system is unstable, that is, flocculated, because of the low hydration and small equilibrium distance of the hydrogen ion. The combined effect of these factors causes the complete neutralization of the charge on the kaolinite particle, their kinetic energy impels them toward each other, and they collide to form aggregates and flocculate. This action agrees with the results of Hauser and Hirshon,[40] who state that "for maximum gelation effects, an ion directly opposite the one preferentially adsorbed by the colloid will produce the best results."

(2) Ion Exchange Reactions

With the picture of a clay OH-H particle established, the reactions next considered are those which occur on the addition of various electrolytes to this particular form of the particle of kaolinite. Kondo[16] states that the addition of alkalis to the electrodialyzed kaolinite complex causes the cation of the electrolyte to replace the hydrogen countercharge of the kaolinite micelle. This is the familiar base-exchange reaction which may be represented by equation (1),

$$\text{Clay OH-H} + \text{NaOH} \longrightarrow \text{clay OH-Na} + \text{H}_2\text{O} \quad (1)$$

The reaction will proceed to the right because of the establishment of a system with a lower free energy; the exchange occurs here between the hydrogen counterions of the kaolinite complex and the added sodium ions of the electrolyte (Fig. 16 shows such a micelle). This reaction is the same for all types of alkalis added, that is, the cation of the electrolyte now becomes the counterion of the kaolinite particle, and the hydrogen ion, which formerly was the countercharge, combines with the hydroxyl ion left by the sodium to form undissociated water. The pH value of the system should change only to the extent that this newly formed sodium clay increases its charge, that is, for every Na^+ ion existing outside the water hull, one of the adsorbed OH^- ions will not be neutralized so that the concentration of the hydroxyl ions in the system will correspondingly increase. The pH will thus depend on the charge of the particle at this point. In the case of the clay OH-H particle, all of the hydrogen counterions occur

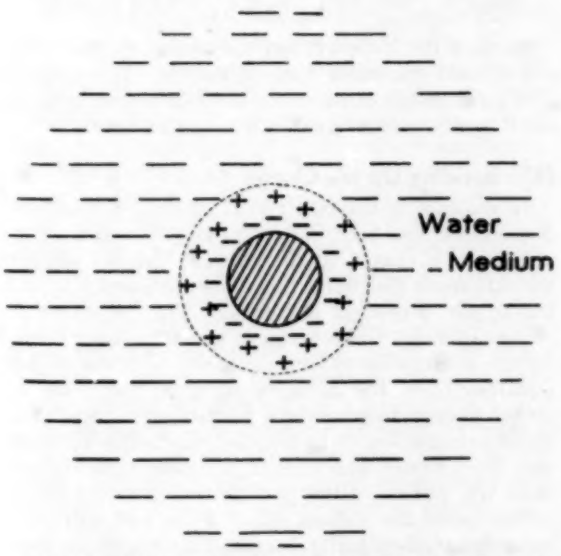

FIG. 15.—Schematic representation of the micelle of an electrodialyzed kaolinite particle in a water medium; the hydroxyl ion is represented by the negative signs and the hydrogen counterion by the positive signs.

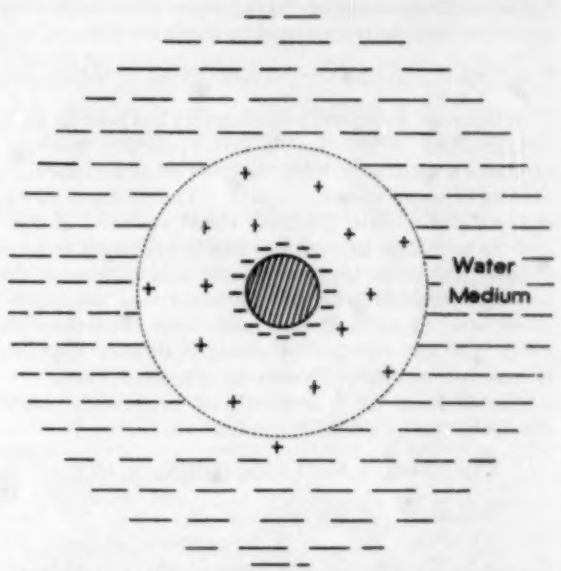

FIG. 16.—Schematic representation of the micelle of a clay OH-Na particle in a water medium; sodium = (+); hydroxyl group = (−).

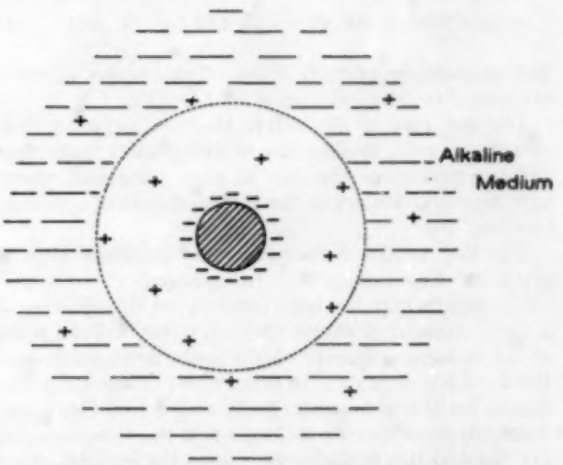

FIG. 17.—Schematic representation of the micelle of a clay OH-Na particle in an alkaline medium; sodium = (+); hydroxyl group = (−).

within the water hull, that is, the particle has a zero charge. The theoretical pH of such a system should be 7 pH or that of pure water. This condition is not realized in the experimental work because the distilled water used has a pH which varies from 5.5 to 5.9, and the clay, furthermore, may contain small traces of soluble salts which would tend to lower the resulting pH of the system to a 5.3 value. The point to be emphasized, however, is that the clay OH-H particle exchanges its hydrogen ions for the sodium ions of the alkali added so that the pH of the system changes only to a limited degree and this kaolinite therefore exhibits a type of buffer action. When the exchange reaction is completed, a further addition of the electrolyte will produce equal amounts of Na^+ and $(OH)^-$ ions in the medium (Fig. 17 depicts such a micelle).

The exchange reaction taking place when basic salts are added may be represented by equation (2).

$$2\ \text{clay OH-H} + Na_2SiO_3 \longrightarrow 2\ \text{clay OH-Na} + H_2SiO_3 \quad (2)$$

In this case, as before, a sodium clay has been formed. The product of the double decomposition, however, produces a weak acid, which in this case is the unstable, extremely weak metasilicic acid. The addition of excess sodium silicate produces equal amounts of Na^+ and SiO_3^{--} ions in solution, which hydrolyze to form sodium hydroxide and metasilicic acid. Because the sodium hydroxide, which is a stronger base than metasilicic acid, is an acid and more than neutralizes its effect, the net result is a strongly alkaline medium, that is, it contains an abundance of hydroxyl ions.

The addition of a neutral salt produces a slight change in the by-product, equation (3).

$$\text{Clay OH-H} + NaCl \rightleftharpoons \text{clay OH-Na} + HCl \quad (3)$$

The formation of the sodium clay again has been brought about, but, as a by-product, an acid will always be the result. This trace of acid should be detectable from the titration results (see Fig. 11).

The addition of an acid salt causes the exchange reaction shown by equation (4).

$$\text{Clay OH-H} + NH_4Cl \rightleftharpoons \text{clay OH-}NH_4 + HCl \quad (4)$$

The decrease in the pH value of this series again is attributed to the formation of HCl (see Fig. 11).

The last type of electrolyte that can be conceived, namely, an acid, would cause no exchange of the hydrogen counterions of the clay to take place and, therefore, no marked effect on the system should be apparent (see Fig. 10).

The key to the deflocculation of kaolinite slips is given by these equations. In equations (1), (2), and (3), a sodium clay has been formed, but the addition of a slight amount of excess electrolyte beyond the point of the exchange capacity results in the deflocculation of the kaolinite slips only in equations (1) and (2). The reason for this is apparent from a chemical viewpoint. Where hydroxides are used in the first reaction, equation (1), the addition of the excess causes the medium of the system to become alkaline by virtue of the hydroxyl-ion concentration. In the second reaction, equation (2), the basic salts added in excess will hydrolyze, thereby increasing the (OH)-ion concentration. In the case of the neutral or acid salt, the exchange reaction has produced an acid, shown by equations (3) and (4). With the addition of an excess of the neutral salt, it hydrolyzes and produces equal amounts of H^+ and OH^- ions, but the acid has already been produced by the exchange reaction. The acid medium is the only factor to which can be attributed the difference in viscosity relations of these samples on the addition of the three types of electrolyte. The hydrolysis of the acid salt will yield a preponderance of H ions which should result in a decrease in the pH value of the system (see Fig. 11). From a chemical standpoint, therefore, deflocculation of the clay OH-H (hydrogen clay) will result on the formation of a clay OH-Na (sodium clay) in the presence of an alkaline medium.

A corollary to the observation by Hauser and Hirshon[46] might be stated as follows: For maximum stability of a sol, the same ions are necessary in the medium as those preferentially adsorbed by the colloid. This is in accord with the Ostwald[47] theory that the medium is an important factor when considering the stability of a colloidal system.

Before proceeding to an explanation of the effect of the cation on the degree or extent of deflocculation, some thought must be given to the replacement of the hydroxyl ion that is preferentially adsorbed by the kaolinite particle. The kaolinite particle, according to the Fajans-Hahn law, has been shown to have a decided preference for the hydroxyl ion. This would hold only for low concentrations where the mass effect could be neglected. If, on the other hand, high concentrations of certain other anions were associated with the clay OH-H particle, an exchange of anions might conceivably take place and the adsorbability would follow the Hofmeister series,

$$SO_4 < F < NO_3 < Cl < Br < I < CNS < --OH.$$

Because the hydroxyl ion, according to this series, would yield the stable form of the clay, it is unlikely that an exchange of the anion has taken place with the small concentrations used in these experiments.

(3) Building Up the Charge

In the case of the clay OH-H (hydrogen kaolinite), flocculation has been shown to be the result of the absence of a charge on the particle, and the effect of the cations on the charge must be established. According to the preceding paragraphs, Fig. 16 shows the picture of a clay OH-Na micelle which has been formed by the addition of sodium hydroxide to a clay OH-H, equation (1). The negative signs represent the adsorbed hydroxyl ions and the positive signs those of the sodium counterions. In this case, the medium is water, and the solvated hull extends a considerable distance from the surface of the particle owing to the greater hydration of the sodium ions.[46] The hull entraps all but a few of the countercharges (Fig. 16), which would

[46] E. W. Washburn and E. B. Millard, "Ionic Hydration and Transference Numbers of Caesium Chloride," *Jour. Amer. Chem. Soc.*, **37**, 694 (1915).

be the ideal case mentioned by Mattson[47] and would represent the maximum "swelling" of the particle. The charge on the particle or zeta potential, ζ, may be calculated by means of the Helmholtz equation,

$$\zeta = \frac{4\pi e d}{D}$$

Where e = electric charge.
d = thickness of double layer.
D = dielectric constant of medium.

For the system as represented in Fig. 16, a definite value for ζ will be forthcoming.

If a slight excess of sodium hydroxide now be added to the system, the decrease in the thickness of the double layer, d, resulting from the reduction of the solvated hull as explained on the basis of the Donnan equilibrium[48] and shown by Mattson,[47] may be neglected. The decrease, however, in the dielectric constant, D, of the medium will be appreciable, owing to the presence of the electrolyte. The increase in concentration of the hydroxyl ions of the system, furthermore, may force these ions to enter the micelle and become adsorbed onto the kaolinite surface. In this manner, the density of the electric charge, e, is increased. The combination of these two changes, that is, (1) the increase in e, and (2) the decrease in D, will cause a significant increase in the charge on the particle, ζ, as calculated by the Helmholtz equation.

Such a system may be represented as shown in Fig. 17. Because of the change in the dielectric of the medium, the countercharges in this case are able to exhibit their maximum equilibrium distances and the number of sodium countercharges located within the solvated water hull (represented by the dotted line in Fig. 17) is therefore considerably smaller. Additional hydroxyl ions, as has been said, may also be adsorbed by the particle because of the increased concentration of these ions in the medium. The combined effect of the changes in the system is to cause the kaolinite particle to obtain a higher net negative charge. The charged particles repel each other electrostatically, and the system is dispersed and at its point of maximum stability.

The equilibrium distance of the countercharges controls the net charge possible on the particle. Thus, if this equilibrium distance is smaller for some particular cation under similar conditions, the result would be manifested in a smaller charge, owing to the neutralization of the adsorbed ions, and the degree of deflocculation, therefore, would be correspondingly reduced. Hofmann and Bilke[39] have shown that the equilibrium distances of the cations increase as the valency of the cation decreases except for hydrogen which has the smallest equilibrium distance (see Fig. 1). The monovalent ions would be expected, on this basis, to produce the maximum charge on the particle and therefore the maximum degree of deflocculation; the divalent ions would produce somewhat smaller effects; the trivalent cations, an even smaller charge; and hydrogen, no charge and complete instability. This theory agrees with the Hardy-Schulze[2] valency rule and also with the experimental results. It explains, furthermore, why the adsorption of the aluminum ion on the active spots of the crystal fragment would result in the flocculation of the system as well as the wide use of polyvalent cations as coagulants.

It has thus been established that (*a*) *the charge on the kaolinite particle controls the degree of deflocculation and is governed by the type of cation and* (*b*) *the stability of the system is controlled by the anion of the medium and is governed by the type of anion preferentially adsorbed.* In other words, if a colloidal particle for some reason adsorbs the sulfate radicle on its active surface, the system should then exhibit maximum stability when the proper cation serves as the counter charge and when the SO_4 group is present in the medium. Because maximum stability of these kaolinite slips results when excess hydroxyl ions are added (with the proper type of cations) to the medium, if the preceding statement is true, it is logical to deduce that the hydroxyl ion is preferentially adsorbed.

(4) Electrical Forces and Effect on Viscosity

With the aid of electrical forces associated with a given colloidal system (Hauser and Hirshon[49]), the reasons for the viscosity relations as they occur in a kaolinite slip, such as that studied here, may be visualized. The clay OH-H particle is an anomalous case, however, and the picture of the electrical forces can show why the system is unstable. Figure 18 shows the electrical forces associated with such a particle of kaolinite in a water medium. Curve *A* represents the rate of decline of the electrical forces of attraction due solely to the hydroxyl ions that give the negative charge to the particle. Curve *R* represents the rate of decline of the electrical forces of repulsion associated with the diffuse double layer and resulting from the hydrogen counterions. These repulsion forces are extremely

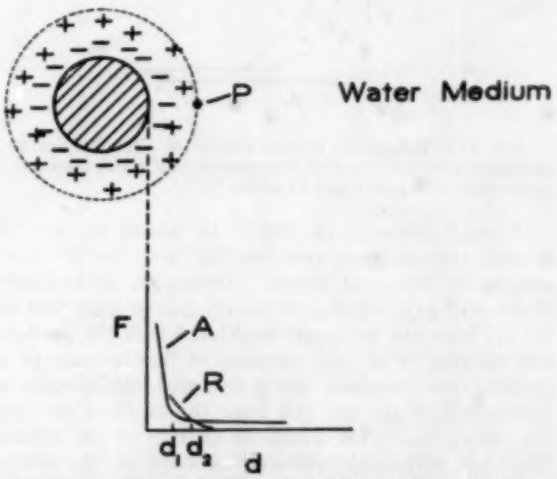

FIG. 18.—Schematic representation of electrical forces associated with a clay OH-H particle in a water medium, according to Hauser and Hirshon.[49]

[47] S. E. Mattson, "Laws of Soil Colloidal Behavior: Forms and Functions of Water," *Soil Sci.*, **33** [4] 301–23 (1932); *Ceram. Abs.*, **11** [8] 469 (1932).

[48] T. R. Bolam, The Donnan Equilibria. George Bell and Sons, Ltd., London, 1932.

weak, if they are present at all because the charge on the particle is assumed to be zero. Distance, d_1, represents the center from which all ions of the diffuse double layer may be considered to be acting. At some distance, d_2, P represents the point where the charges of the diffuse double layer approach zero, and the position of these points may vary, depending on the medium and the equilibrium distance of the countercharges. This theory agrees with the Gouy-Freundlich concept, inasmuch as some of the countercharges are considered to be floating about at random in the dispersion medium. The lyosphere, associated with the particle in this case (Fig. 18), relatively speaking, does not extend over a great distance from the surface of the particle. Point P, where the charges of the diffuse double layer approach zero, occurs either within or immediately adjacent to the edge of the lyosphere. In other words, ζ, the charge on the particle, is zero or very nearly so, as might be concluded from the pH value of the electrodialyzed clay slip. Because the repulsion forces approach a zero value more rapidly than do the attraction forces and because of this location of P, attraction forces exist immediately beyond the lyospheres causing particles to be impelled together owing to their kinetic energy. The system, thus, is not stable, and it is flocculated.

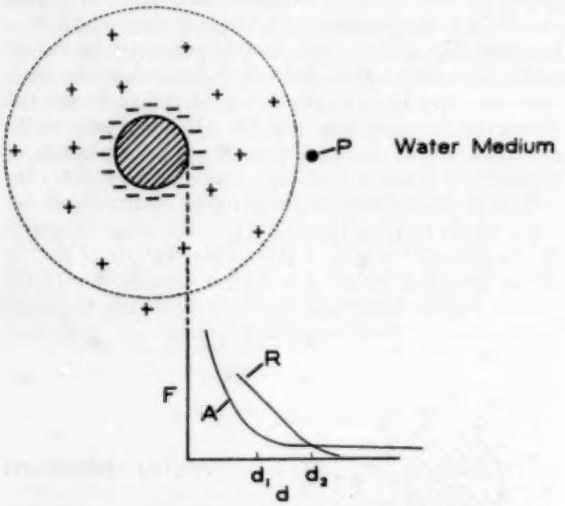

FIG. 19.—Schematic representation of electrical forces associated with a clay OH-Na particle in a water medium, according to Hauser and Hirshon.[49]

If small amounts of NaOH be added to such a system, the exchange reaction Na^+ ions for H^+ ions alters the electrical forces. Owing to hydration[56] of the Na^+ ions, which is relatively greater than that of the H^+ ions, the lyosphere associated with the particle will increase (Fig. 19). Because of this increase in a double-layer thickness, the ζ potential will increase a corresponding amount and have the effect of moving the center line, from which all charges of the diffuse layer are acting, d_1, toward the edge of the newly formed water hull (Fig. 19). Point P therefore will move outward from the surface of the particle so that d_2 of Fig. 19 will be greater than d_2 of Fig. 18. The exchange reaction produces water as a by-product, and the medium may be considered the same as that in Fig. 18 except that a few of the Na^+ countercharges may exist in the medium. If a stress is applied to such a system, shear will occur at the point between the water hull of the kaolinite particle and the medium because this is the only water held to the particle, according to the diffuse double-layer theory.[12] The viscosity of the clay OH-Na particle, which is formed by the addition of 3.0 m.e. of sodium hydroxide as obtained from Fig. 4, is less than that of the clay OH-H particle (170 c.p. vs. 260 c.p.) and it may therefore be assumed that small repulsion forces of an electrical nature possibly exist at this point of shear.

If a slight excess of NaOH is added to this system, pronounced changes will result. The kaolinite particle, in the first place, can no longer exchange H^+ ions for Na^+ ions, and the medium therefore becomes alkaline with the accompanied large increase in the ζ potential (as has been discussed). The effect of this decrease in the dielectric constant manifests itself in the movement of point P to a considerable distance, d_2, beyond the surface of the solid particle (Fig. 20). The increased charge on the particle results in greater repulsion forces between particles being set up. A considerable number of repulsion forces therefore exist immediately adjacent to the boundary of the solvated hull, which has not changed in size appreciably, and these decrease the amount of force needed to shear the system at this point of shear. This would account for the great reduction in the viscosity of the system shown by the results in Fig. 4.

The charge on the particle has been shown in the preceding section to decrease from a maximum charge produced by the monovalent cations through a low charge produced by the trivalent cations to the zero charge which results when hydrogen serves as the counterion.

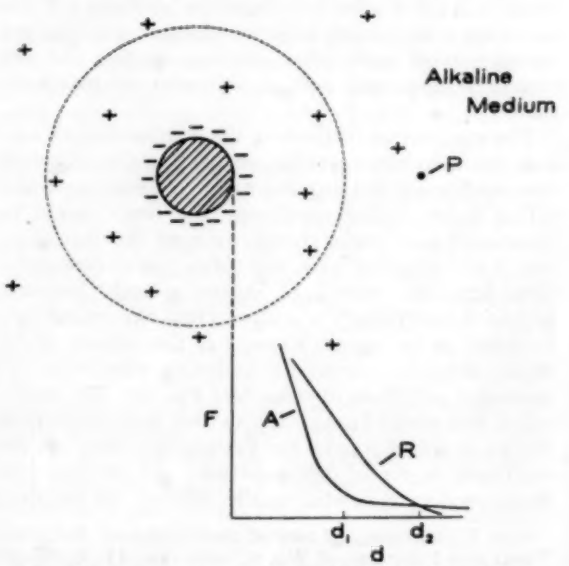

FIG. 20.—Schematic representation of electrical forces associated with a clay OH-Na particle in an alkaline medium, according to Hauser and Hirshon.[49]

The hydration of the cations follows the same sequence as far as can be determined.[56] The equilibrium distance of the cations also varies in the same direction, that is, a maximum equilibrium distance for the monovalent cations and minimum distance for hydrogen, according to Hofmann and Bilke.[39] The total drop in viscosity of such systems therefore should be expected to decrease from the monovalent to the divalent cations. This has been verified by the results. The electrical forces associated with a kaolinite particle, which contains such divalent ions as countercharges, may therefore be represented as shown in Fig. 21.

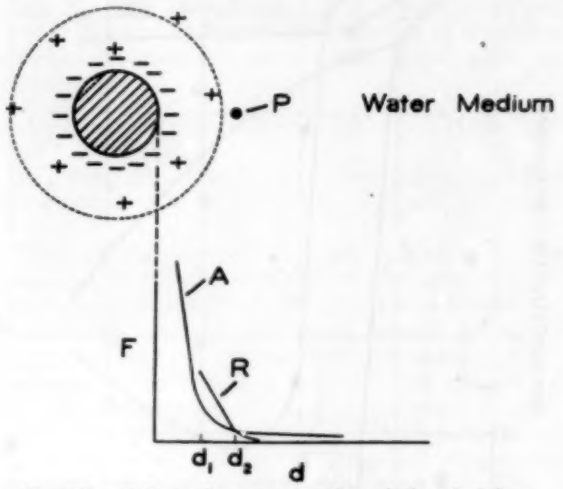

FIG. 21.—Schematic representation of electrical forces associated with a (clay $OH)_2$-Ba particle in a water medium, according to Hauser and Hirshon.[49]

With the further addition of electrolyte, the gelation effects may be explained by means of Fig. 20. The addition of larger quantities of electrolyte causes a reduction in the charge on the particle because the increased concentration of electrolyte in the dispersion medium forces more and more of the sodium countercharges to enter the solvated hull, thus neutralizing the effect of the adsorbed ions as explained by the Donnan membrane equilibrium.[58] This reduction in the charge on the particle would have the effect of reducing the value of the repulsion forces. The introduction of a large excess of electrolyte, according to Mattson,[57] will cause the reduction of the size of the water hull, that is, the "swelling" is reduced. With this decrease in swelling and the reduction of the repulsion forces, Fig. 20 shows that the net repulsion forces now existing outside the water hull are therefore constantly decreasing, and consequently more mechanical energy will be needed in order to produce shear when force is applied to the system.

IV. Practical Considerations

The effect of ions on the electrical forces associated with kaolinite particles has been shown as well as the resulting action of these coulombic forces on the degree of deflocculation of the system. With this knowledge of the mechanism of the process available for dilute kaolinite slips, the results to be obtained on slips at commercial specific gravity values and the effect of soluble salts as present in natural clays must be determined. The highest specific gravity slips possible with single clays are in the region of 1.3 to 1.5 (or between 35 to 55% of solids by weight) because the particle-size distribution of single clays is not properly arranged to give the closest packing and they thereby contain many voids which must be filled by the medium. A ratio of approximately 35% of solids to 65% of water by weight is needed on this basis to cause the slip to flow even under ideal conditions of deflocculation. Tests have been made on slips containing the clean kaolinite used in this work at specific gravity values as high as 1.46 (52% of solids by weight). These results are comparable to the data presented in this paper.

Certain whiteware bodies are in the process of being thoroughly cleaned,[1] and preliminary results indicate a decided improvement in the fluidity of such cleaned slips over the commercial values, that is, the relations found with dilute suspensions will also apply to clean commercial slips.

The effect of soluble salts on the mechanism of deflocculation may therefore be observed on single clays, and the conclusions derived are useful and may be given a practical application. Although it is not within the scope of this paper to present a detailed picture of the

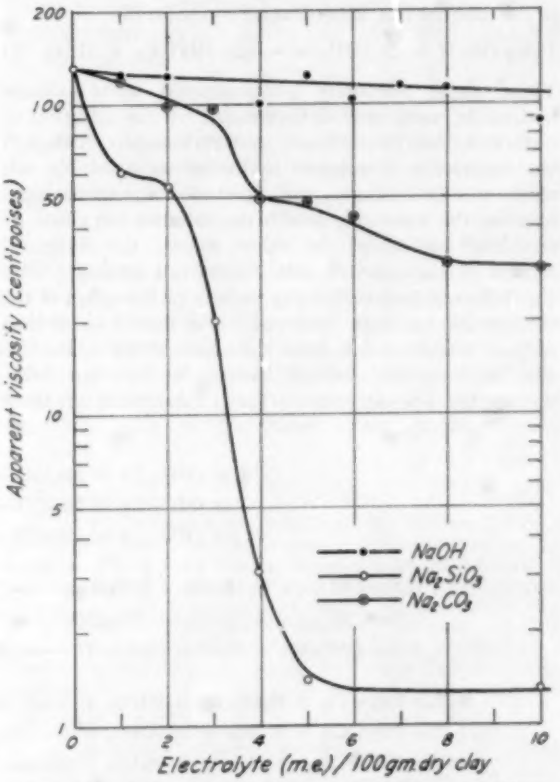

FIG. 22.—Viscosity relations on addition of sodium hydroxide, sodium silicate, and sodium carbonate to an electrodialyzed suspension of kaolinite (16% by weight) purposely contaminated with 0.56% of calcium hydroxide.

effect of soluble salts on the mechanism of the deflocculation process, a relatively simple case will be selected and should serve to illustrate the reasoning to be employed in such a study. The results given in this paper have shown (1) that polyvalent cations decrease the degree of deflocculation of clay slips and that maximum deflocculation results only when monovalent ions are present and (2) that anions, other than the hydroxyl ion, decrease the stability of the system. If, therefore, soluble salts are present in clays and contain ions which fall into either classification, interference with the mechanism of deflocculation is brought about and the degree of deflocculation will be altered and reduced depending on the type of soluble salt present. To counteract the effect of the interfering ions, another method is available (other than actual removal of the soluble salts) and is based on the knowledge of the requirements for complete deflocculation. This second method consists of converting the soluble salts into insoluble salts. Because the mechanism of deflocculation depends on the existence of ions and because soluble salts can ionize, thereby causing interference, the conversion of the salts which dissociate into undissociated salts will render them ineffective.

Figure 22 shows the viscosity relations of samples of clean clay slips to which 0.56% of calcium hydroxide has been added. This addition should cause a calcium clay to be formed because of the greater adsorbability of the calcium ion, according to equation (5).

$$2\ \text{clay OH-H} + \text{Ca(OH)}_2 \longrightarrow (\text{clay OH})_2\text{-Ca} + 2\text{H}_2\text{O}. \quad (5)$$

These slips, purposely contaminated with calcium hydroxide, were next deflocculated by the addition of sodium hydroxide, silicate, and carbonate. Although the occurrence of calcium hydroxide as a soluble salt would not be frequent, this substance was used to determine the means by which the calcium ion could be rendered ineffective; in other words, the hydroxyl radicle of the calcium salt should not interfere with the deflocculation of the slip as long as the effect of the calcium ion has been removed. The results show that sodium silicate and sodium carbonate deflocculate this slip, whereas the sodium hydroxide does not bring about this phenomenon. The explanation of these results is easily available from chemical reasoning (see equations (6), (7), and (8)).

In equations (6) and (7), the formation of insoluble salts causes the reaction to proceed to the right, whereas in equation (8) no reaction will occur because the calcium ion has a greater adsorbability than the sodium ion and refuses to be removed from the clay. The sluggish deflocculating action of sodium carbonate in this test is due to the slight solubility of the calcium

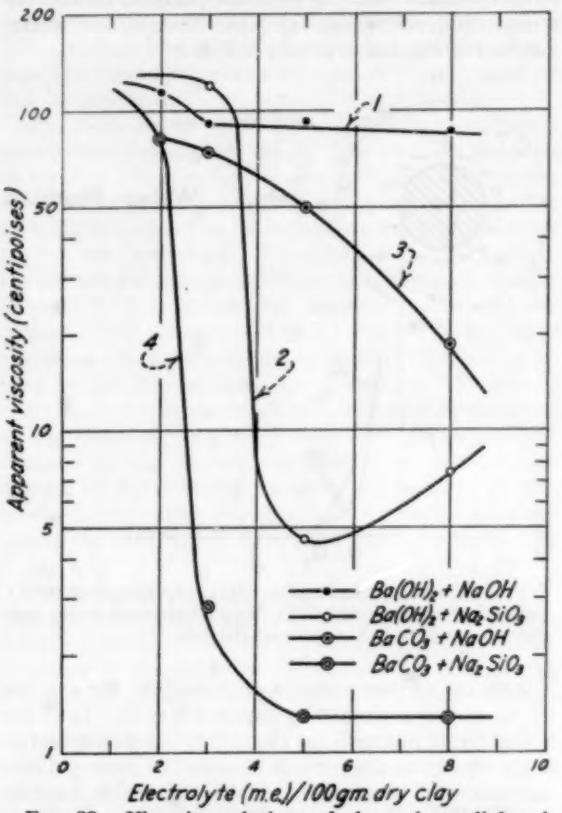

FIG. 23.—Viscosity relations of clean electrodialyzed slips (16% of solids by weight) purposely contaminated with 0.56% of $CaSO_4$ and deflocculated with various electrolytes.

$$(\text{Clay OH})_2\text{-Ca} + \text{Na}_2\text{SiO}_3 \longrightarrow 2\ \text{clay OH-Na} + \textit{CaSiO}_3. \quad (6)$$

$$(\text{Clay OH})_2\text{-Ca} + \text{Na}_2\text{CO}_3 \longrightarrow 2\ \text{clay OH-Na} + \textit{CaCO}_3. \quad (7)$$

$$(\text{Clay OH})_2\text{-Ca} + 2\text{NaOH} \not\longrightarrow. \quad (8)$$

$$(\text{Clay OH})_2\text{-Ca} + \text{H}_2\text{SO}_4 + 2\text{Na}_2\text{SiO}_3 \longrightarrow 2\ \text{clay OH-Na} + \textit{CaSiO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{SiO}_3. \quad (10)$$

$$(\text{Clay OH})_2\text{-Ca} + \text{H}_2\text{SO}_4 + 2\text{Na}_2\text{CO}_3 \longrightarrow 2\ \text{clay OH-Na} + \textit{CaCO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{CO}_3. \quad (11)$$

$$(\text{Clay OH})_2\text{-Ca} + \text{H}_2\text{SO}_4 + 2\text{NaOH} \longrightarrow (\text{clay OH})_2\text{-Ca} + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}. \quad (12)$$

$$(\text{Clay OH})_2\text{-Ca} + \text{H}_2\text{SO}_4 + \text{Ba(OH)}_2 + \text{Na}_2\text{SiO}_3 \longrightarrow 2\ \text{clay OH-Na} + \textit{BaSO}_4 + \textit{CaSiO}_3 + 2\text{H}_2\text{O}. \quad (13)$$

$$(\text{Clay OH})_2\text{-Ca} + \text{H}_2\text{SO}_4 + \text{Ba(OH)}_2 + \text{Na}_2\text{CO}_3 \longrightarrow 2\ \text{clay OH-Na} + \textit{BaSO}_4 + \textit{CaCO}_3 + 2\text{H}_2\text{O}. \quad (14)$$

$$(\text{Clay OH})_2\text{-Ca} + \text{H}_2\text{SO}_4 + \text{Ba(OH)}_2 + 2\text{NaOH} \longrightarrow (\text{clay OH})_2\text{-Ca} + \textit{BaSO}_4 + 2\text{NaOH} + 2\text{H}_2\text{O}. \quad (15)$$

$$(\text{Clay OH})_2\text{-Ca} + \text{H}_2\text{SO}_4 + \text{BaCO}_3 + \text{Na}_2\text{SiO}_3 \longrightarrow 2\ \text{clay OH-Na} + \textit{BaSO}_4 + \textit{CaSiO}_3 + \text{H}_2\text{CO}_3. \quad (16)$$

$$(\text{Clay OH})_2\text{-Ca} + \text{H}_2\text{SO}_4 + \text{BaCO}_3 + \text{Na}_2\text{CO}_3 \longrightarrow 2\ \text{clay OH-Na} + \textit{BaSO}_4 + \textit{CaCO}_3 + \text{H}_2\text{CO}_3. \quad (17)$$

$$(\text{Clay OH})_2\text{-Ca} + \text{H}_2\text{SO}_4 + \text{BaCO}_3 + 2\text{NaOH} \longrightarrow 2\ \text{clay OH-Na} + \textit{BaSO}_4 + \textit{CaCO}_3 + 2\text{H}_2\text{O}. \quad (18)$$

carbonate formed. Complete deflocculation of this slip will not occur until a sufficient number of $CO_3^{=}$ ions have been added to repress the dissociation of the calcium carbonate.* The solubility of the salts of calcium confirm this as follows:

	Gm./100 parts water at 25°C.
$CaSO_4$	0.208
$Ca(OH)_2$	0.112
$CaCO_3$	0.0056
$CaSiO_3$	0.0010

Figure 23 gives the viscosity relations of samples of clean clay slips treated with 0.56% of calcium sulfate. The addition would cause the formation of a calcium clay (see equation (9)), for the same reason given for equation (5).

$$2\ \text{clay OH-H} + CaSO_4 \rightleftharpoons (\text{clay OH})_2\text{-Ca} + H_2SO_4. \quad (9)$$

If sodium silicate, carbonate, or hydroxide be added to these samples, the reactions (10), (11), and (12) might occur.

The calcium ions would be made ineffective by the formation of calcium silicate or calcium carbonate, as shown in equations (10) and (11). No effective deflocculation, however, could result because the sulfate radicle has not been rendered ineffective and the proper deflocculant has not been formed. The addition of sodium hydroxide has no effect on the removal of the Ca^{++} or the $SO_4^{=}$ ions. If, however, barium hydroxide be added before adding the dispersing agents, the reactions (13), (14), and (15) would occur.

The addition of barium hydroxide produces barium sulfate, which is slightly soluble (0.00012 gm. per 100 parts of water), and renders the barium and sulfate ions ineffective. By the addition of sodium silicate or sodium carbonate, the calcium ion would be converted to an insoluble form and deflocculation could proceed normally (see equations (13) and (14) and curve 2, Fig. 23). Sodium hydroxide would not remove the interfering calcium ion and no deflocculation should result (see equation (15) and curve 1, Fig. 23). If the correct amount of barium carbonate were used, the calcium, barium, and sulfate ions would be rendered ineffective according to equations (16), (17), and (18).

Sodium hydroxide, silicate, or carbonate could be used in this case to deflocculate the slip; the results (curves 3 and 4, Fig. 23) show why barium carbonate is widely used in the deflocculation of commercial slips.

It is also clear now why sodium hydroxide is not used commercially as a deflocculant and why sodium silicate or sodium carbonate is used instead. The hydroxides of the alkaline earths are more soluble than the corresponding silicates or carbonates. The use of sodium hydroxide would form the hydroxides of these elements and thereby fail to render them totally ineffective. These results show that when Ca^{++} ions are present with clays, sodium silicate will deflocculate the clay better than sodium carbonate owing to the greater solubility of the calcium carbonate over the calcium silicate. If Mg^{++} ions, however, are present as soluble salts, sodium carbonate should be as effective as sodium silicate on the basis of solubility data. These simple tests serve to emphasize the effect of minute traces of interfering ions in connection with the deflocculation process.

Depending on the type of soluble salt present, suitable deflocculation could be arrived at by simple chemical reasoning based on the solubilities of various salts. The use of tannates, gallates, phosphates, and the host of other miscellaneous electrolytes of organic or inorganic nature as dispersing agents could be explained in detail, based on the knowledge of the type of soluble salt present and on the solubilities of the several combinations. Such an explanation could not be attempted in this report. Instead of a hit-and-miss study of deflocculants, it would be wiser (as has been shown) to determine carefully the type and amount of soluble salt present in a given body and then to work out carefully the proper dispersants to be used in the deflocculation of the slip. Olmstead[10] and his collaborators brought out this technique several years ago in connection with the dispersion of soils.

A thorough understanding of the mechanism of deflocculation has been made possible by the study of a carefully cleaned sample of kaolinite. The effect of the other variables mentioned in Part I,[1] namely, associated organic or mineralogic impurities, surface area, and adsorbed gases, is in the process of study and will be reported soon.

V. Conclusions

If is it assumed that kaolinite develops active areas on the formation of colloidal particles resulting from fracture parallel to the *c*-axis, which areas are then capable of preferential adsorption of the hydroxyl group, the following conditions must be fulfilled in order that maximum dispersion of clean slip results: (1) monovalent cations must serve as the countercharges and (2) the medium must contain a slight excess of hydroxyl ions, that is, it must be alkaline.

With the knowledge of the mechanism of deflocculation presented here, the reasons for the inconsistent behavior of clays may be traced, in part, to the presence of soluble salts.

Acknowledgment

E. A. Hauser has aided greatly in the interpretation of these results, and his cooperation is acknowledged by the authors. This work has been made possible because of the financial assistance of the following organizations: Edgar Brothers Company, Findlay Clay Products Company, General Ceramics Company, General Electric Company, Georgia Kaolin Company, H. C. Spinks Clay Company, and Vitreous China Plumbing Fixtures Association.

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* See also conclusion (*c*) under Results in section II (2), pp. 193–94.

[10] L. B. Olmstead, L. T. Alexander, and H. E. Middleton, "Pipette Method of Mechanical Analysis of Soils Based on Improved Dispersion Procedure," *U. S. Dept. Agr. Tech. Bull.*, No. 170 (1930); *Ceram. Abs.*, **9** [7] 581 (1930).

SPECIFIC HEATS OF CHROME AND MAGNESIA REFRACTORIES*

By Gilbert E. Seil, Frank G. Heck, and H. A. Heiligman†

Abstract

The previous work in the field is surveyed, the method of preparing the samples is described, and chemical, petrographic, and screen analyses and photomicrographs of the samples are presented. Specific-heat determinations were made by the method of mixtures in a calorimeter using carbon tetrachloride; the calorimeter and the auxiliary equipment are described; and the procedures for determining the heat capacity of the calorimeter system and for the specific heats of the test samples are given in detail. The results are summarized, tabulated, and compared with published data. In addition to the bibliography of the papers mentioned in the article, an additional section (Section B), which served as a background for the study, is included.

I. Introduction

A survey of the literature covering the specific heats of refractory materials reveals an astounding lack of complete and detailed information describing the refractory materials on which the determinations were made. Too much emphasis cannot be placed on the fact that in the publication of research information for the advancement of knowledge, and for the stimulation of further investigation it is essential that there be a complete description of the pertinent properties of the materials investigated, and specific, rather than general, discussions of the treatment of the materials during the investigation.

In the development of refractory products made from chrome ore in the present study, data were obtained on the effect of heat treatment and chemical correction on the chemical and physical properties of the commercially available chrome ores. One phase of this work consisted in determining the mean specific heats between 25° and 850°C. of chrome ore (1) physically improved by heat treatment, and (2) physically and chemically improved by chemical correction and heat treatment. The specific heat at 850°C. of a low-iron, domestic magnesite, which was specially heat treated, was also determined.

II. Survey of Previous Work‡

Few references on the specific heats of chrome ore and commercial chrome refractories are found in the literature. The available data have limited significance for practical purposes because of insufficient or total absence of information concerning the chemical and physical characteristics of the materials tested and the various conditions under which the materials investigated were prepared. Determinations of the specific heat of chrome ores have been made or referred to by Tadokoro,[8] Rees,[10] Singer,[11] Green,[13] and Bazilevich.[20,21]

The specific heat of pure or relatively pure magnesium oxide has been determined by Regnault,[1] Russel,[2] Magnus,[3] Steger,[5] Parks and Kelley,[15] and Wilkes.[19]

Investigations of the specific heat of commercial magnesite products have been made by Heyn, Bauer, and Wetzel,[4,7] Steger,[5] Tadokoro,[8,12] Green,[9,13] Rees,[10] Singer,[11] Hartmann and Westmont,[14] Cohn,[16,17] Wagner,[18] Bazilevich,[20,21] and Mita.[22]

Most of the determinations noted have been made by the method of mixtures in one modification or another, using a water calorimeter. Wide variations in the methods of preparation and in the chemical analyses of the materials investigated undoubtedly account for a major portion of the divergence of the results observed.

III. Preparation of the Materials

Chrome ore No. 1 was prepared by heat-treating crude chrome ore at 1870°C. in an oxidizing atmosphere in an oil-fired rotary kiln. On cooling, a stabilized product is obtained in which the chemical and physical rearrangements are in equilibrium and from which the shrinkage has been removed. The primary component, chromite, is completely recrystallized physically. This change, particularly if the chromite crystals are much increased in size, decreases their chemical reactivity because it decreases the surface available for chemical action. The secondary component, consisting originally of impure magnesium silicates of variable composition, is converted from a variable crystalline structure to a product of glassy character, substantially homogeneous and with a softening range in contrast to a sharp melting point.*

For chrome ore No. 2, crude chrome ore, prepared as chrome ore No. 1, was reduced to a grind with a mesh-ratio suitable for briquetting; 77½ parts by weight of this grind were mixed thoroughly with 22½ parts by weight of crystallized magnesia in the form of finely ground periclase. The mixture was briquetted and fired at 1870°C. in an oxidizing atmosphere in an oil-fired tunnel kiln. The conversion of the thoroughly

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† Technical director, ceramic engineer, assistant technical director, respectively, of E. J. Lavino and Company, Norristown, Pa.

‡ For footnote references throughout, see the Bibliography, Section A, p. 210.

* Patents have been issued on this subject to G. E. Seil (E. J. Lavino and Co.) as follows: (1) Chromite Material and Method of Making Same, U. S. 2,028,017, Jan. 14, 1936; and (2) Recrystallization of Chrome Ore, France 781,276, Feb. 18, 1935; Italy 331,458, Nov. 6, 1935; Canada 355,204, Jan. 7, 1936; and Great Britain 451,493, Aug. 4, 1936.

distributed, glassy secondary component (substantially $MgO \cdot SiO_2$) of chrome ore No. 1 to forsterite (magnesium orthosilicate, $2MgO \cdot SiO_2$) is accomplished by this treatment. Forsterite has a melting point of approximately 1910°C. in the pure state, but in the presence of an excess of magnesia, fusion of the compound is not complete at 2040°C. Chrome ore No. 2, therefore, was physically and chemically corrected material in which each grain of recrystallized chromite was completely surrounded by crystallized and bolstered forsterite.*

The domestic magnesite ore was prepared by heat-treating the ore at 1730°C. in an oxidizing atmosphere in an oil-fired rotary kiln. On cooling, a stabilized product was obtained, which had substantially no residual shrinkage and consisted of a primary component of crystallized periclase and well-distributed secondary components of forsterite ($2MgO \cdot SiO_2$) and monticellite ($CaO \cdot MgO \cdot SiO_2$).

Each of the prepared ores was reduced to a grind which had a mesh-ratio suitable for briquetting. Screen analyses of the ground materials are given in Table I.

TABLE I

SCREEN ANALYSES OF GROUND MATERIALS

	Chrome ore (%)		Magnesite ore (%)
	No. 1	No. 2	
Through 8- on 20-mesh	37.36	37.16	46.92
Through 20- on 100-mesh	28.36	30.00	22.16
Through 100-mesh	34.28	32.84	30.92

Using a minimum of organic binder, each ground ore was tempered and pressed into briquettes; these were fired in an oxidizing atmosphere in an oil-fired tunnel kiln as follows: chrome ore No. 1 to cones 16 and 18, approximately 1450° and 1485°C., respectively; chrome ore No. 2 to cones 32 and 34, approximately 1700° and 1760°C., respectively; and the magnesite to cones 26 and 28, approximately 1595° and 1615°C., respectively.

The chemical and petrographic analyses of the fired ores are given in Table II, and Figs. 1, 2, and 3 show photomicrographs of the fired ores.

In order to obtain a maximum uniformity of heat distribution throughout the test sample before its introduction into the calorimeter, samples were used consisting of grains which passed an 8-mesh (National Bureau of Standards screen opening of −0.093 in.) and were retained on 12-mesh (opening −0.065 in.). Approximately 20 lb. of each of the fired ores were crushed in such a manner as to yield a maximum amount of through 8- and on 12-mesh particles. The crushed samples were screened, and the material obtained in each case was washed free of dust and ignited to constant weight at 900°C. The samples, after cooling, were used to determine their mean specific heats between 25° and 850°C. by the method of mixtures.

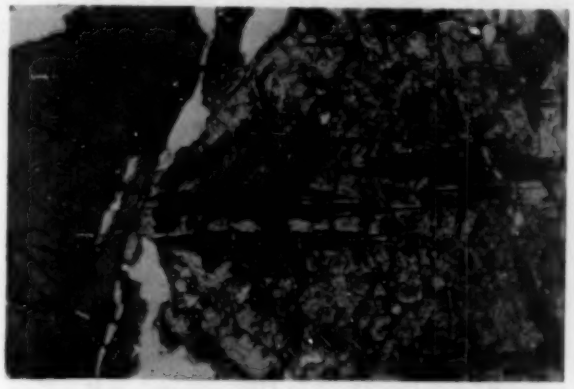

FIG. 1.—Chrome ore No. 1.

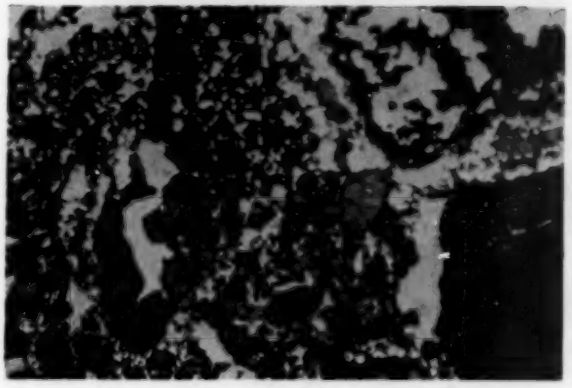

FIG. 2.—Chrome ore No. 2.

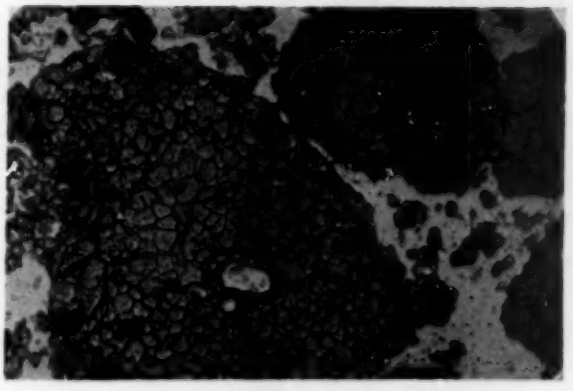

FIG. 3.—Magnesite ore.

* Patents have been issued on this subject to G. E. Seil (E. J. Lavino and Co.) as follows: (1) Chromite Refractory Materials, Belgium 396,089, June 30, 1933; Canada 335,266, Aug. 29, 1933; France 755,038, Nov. 18, 1933; Italy 314,924, Feb. 9, 1934; Great Britain 409,130, April 26, 1934; U. S. 2,028,018, Jan. 14, 1936; and Germany 676,006, March 16, 1939; (2) Method of Making Chromite Refractories, U. S. 2,037,600, April 14, 1936; and (3) Process of Making Chromite Refractories, Belgium 417,817, Oct. 8, 1936; U. S. 2,060,697, Nov. 10, 1936; Italy 345,818, Jan. 16, 1937; France 811,670, April 20, 1937; Canada 366,039, May 11, 1937; and Great Britain 468,659, July 9, 1937.

IV. Method and Apparatus

(1) Method of Mixtures

The method of mixtures is generally acknowledged to be the most accurate for the determination of the specific heats of fired refractory materials which undergo no irreversible thermal changes on heating. In this method, a weighed sample of the material on which the mean specific heat is to be determined is heated to a definite temperature and dropped into a calorimeter containing a weighed amount of a liquid, usually water. The quantity of heat in the material at the time of dropping is determined by measuring the rise in the temperature of the liquid, and the mean specific heat is calculated from the rise in temperature of the liquid, the heat capacity of the system, and the weight and temperature of the sample.

Although water is usually used in the calorimeter, carbon tetrachloride was used in this investigation to preclude the possibility of complete or partial hydration of the magnesia and magnesium compounds in the ores. The carbon tetrachloride was filtered through calcium chloride and redistilled after each determination to eliminate the possibility of error because of potential moisture absorption.

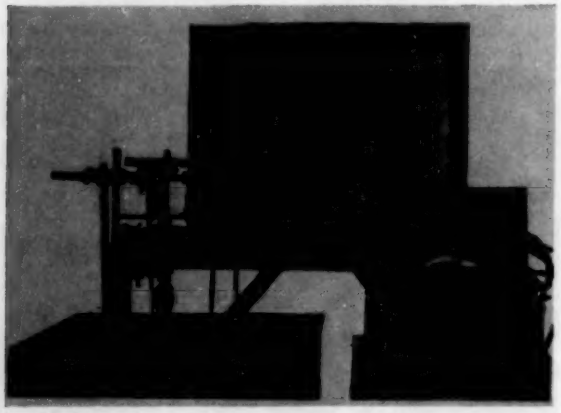

FIG. 4.—The furnace.

(2) The Furnace

The test sample was heated in a refractory casserole in a Nichrome wire-wound silicon carbide muffle (7.5 in. wide, 14.0 in. deep, and 5.5 in. high inside dimensions). The furnace (Fig. 4) was well insulated on all sides to insure uniformity of temperature within the muffle. A snug-fitting counterbalanced door which could be easily raised and lowered formed the front end of the furnace muffle.

(3) The Calorimeter

The calorimeter (Fig. 5) consists of a cylindrical Pyrex-brand glass jar (*A*) of approximately 39 liters capacity ($^5/_{16}$ in. thick, 1 ft. in diameter, and 2 ft. high), surrounded by a layer of exfoliated vermiculite insulation (*B*), and inclosed in a wooden case 20 in. long, 20 in. wide, and 31 in. high (*C*), as shown in Figs. 4 and 5. The stirring apparatus consists of a Pyrex-brand glass shaft (*D*), with two propellers (*E*) inserted in a steel chuck (*F*) and driven by a $^1/_4$-h.p. motor (*G*). Bearings for the stirring shaft and a stand (*H*) and clamp to support the Beckmann thermometer (*T*) are mounted on the lid (*L*) of the calorimeter. The removable lid is held tightiy in place by a gate hook and eye on each side of the wooden case. The rim of the glass jar fits snugly into a channel (*M*), $^1/_2$ in. deep, which is cut in the lid of the calorimeter. The opening (*O*) in the lid of the calorimeter, through which the charge is dropped, is 3.5 in. square. This opening is closed by a wooden plug (*P*), the bearing surface of which is faced with a rubber gasket. A copper-screen basket (*R*) rests on a low, cross-shaped Pyrex-brand glass-rod stand (*S*) on the bottom of the calorimeter to catch the grains of the material being tested. Free circulation of the carbon tetrachloride around the charge is thus made possible, and contact of the hot charge with glass is avoided.

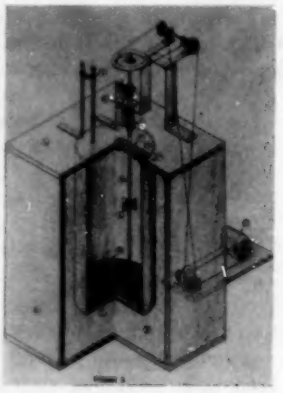

FIG. 5.—The calorimeter.

(4) Temperature Measurements

The temperature of the test sample in the casserole within the furnace was measured by a thermocouple

TABLE II

CHEMICAL AND PETROGRAPHIC ANALYSES OF THE TEST MATERIALS

Chemical analysis	Chrome ore (%)				Magnesite ore (%)
	No. 1		No. 2		
Cr_2O_3	41.47		33.12		
FeO	15.31		12.55		
Fe_2O_3					0.88
Al_2O_3	18.83		14.30		1.29
SiO_2	7.66		7.05		3.85
CaO	0.98		1.18		2.14
MgO	15.56		31.45		91.46
Petrographic analysis					
Primary component	Chromite 85.46		Chromite	67.37	Periclase 87.83
Secondary "	Heterogeneous Ca and Mg silicates	14.35	Periclase	15.43	Monticellite 5.97
			Forsterite	13.56	Forsterite 3.65
			Monticellite	3.29	

inserted through a small hole in the center of the counterbalanced door so that the end of the thermocouple was in contact with the test sample. The thermocouple was a standard platinum, platinum-10% rhodium thermocouple, calibrated specifically for the tests. The electromotive force was read with a Thwing portable potentiometer.

The rise in temperature of the carbon tetrachloride in the calorimeter was measured with a Beckmann differential thermometer (T, Fig. 5), which has a range of 5.5°C. It was graduated in hundredths of a degree and calibrated against a thermometer certified by the National Bureau of Standards. The initial temperature of the calorimeter was approximately 25°C., which coincided with the temperature of the room to within a few tenths of a degree; the final temperature, after inserting the test sample, was approximately 28° to 29°C.

V. Experimental Procedure

(1) Fundamental Data

Weight of CCl_4 (sp. gr. is 1.585) in calorimeter = 53,890 gm.
Weight of metal tube = 555.1 gm.
Specific heat of metal tube = 0.1110 cal./gm./°C. at 60°C.
Weight of distilled H_2O in metal tube = 1000 gm.
Specific heat of H_2O at 60°C. = 0.9989 cal./gm./°C. (International Critical Tables, Vol. 7, p. 232).
Beckmann thermometer 0.000° = 24.290°C.

(2) Heat Capacity of Calorimeter System

Because it was necessary to determine the heat capacity of the calorimeter system as accurately as possible to insure reliable results in later determinations, the method and results of this determination are fully explained.

Approximately 34 liters of carbon tetrachloride, weighing 53,890 gm., were stirred in the calorimeter for 10 minutes, during which time the temperature was read on the Beckmann thermometer every minute. When the rate of temperature change, as measured on the Beckmann thermometer, remained constant for 10 minutes, a weighed metal tube at 60°C. was inserted quickly into the calorimeter with continual stirring. A seamless steel tube, sealed at one end, was used. The rise in temperature was observed every minute until the rate of temperature change remained constant over a suitable rating period. The time-temperature curves were plotted as shown in Fig. 6.

Under the conditions existing in the procedure, the temperature of the liquid in the calorimeter never becomes constant but rises or falls depending on the temperatures of the room and of the calorimeter system. The stirring of the liquid, both before and after the insertion of the metal tube (or the sample), is carried out only until the rate of rise or fall in temperature becomes constant. Knowing that the rate of temperature change has become constant, the experimenter can leave the calorimeter long enough to withdraw the sample from the furnace, insert it into the calorimeter, and know the exact temperature at the time of insertion merely from an observation of the time. The exact

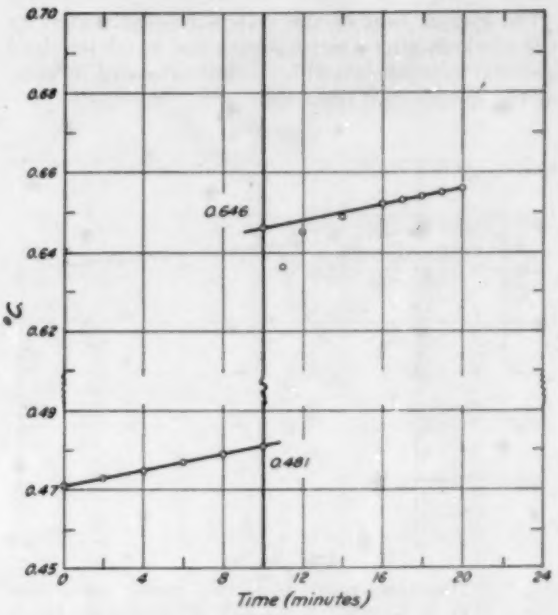

FIG. 6.—Time-temperature correction curve; metal tube at 60°C. inserted in CCl_4; determination No. 1.

temperature rise is determined by projecting the curves showing the constant rates of change before and after insertion of the tube (or of the sample) (Fig. 6).

An average of ten determinations showed the rise in temperature, due to the insertion of the metal tube, to be 0.163°C.

The same amount of carbon tetrachloride (53,890 gm.) was again stirred in the calorimeter and the temperature was noted every minute until the rate of temperature change remained constant for 10 minutes. The metal tube at 60°C., containing 1000 gm. of distilled water at 60°C., was then inserted quickly into the calorimeter with continual stirring. The rise in temperature was noted at one-minute intervals over a suitable rating period, and the temperatures were plotted (Fig. 7). An average of four determinations showed the rise in temperature (due to the insertion of the metal tube at 60°C. containing 1000 gm. of distilled water at 60°C.) to be 2.535°C.

The heat capacity of the calorimeter system may be calculated in two ways as follows:

$$C_{MT \text{ at } 60°C.} W_{MT(60-T)} + C_{H_2O \text{ at } 60°C.} W_{H_2O(60-T)} = CW(T - t). \quad (1)$$

Wherein $C_{MT \text{ at } 60°C.}$ = sp. ht. of metal tube at 60°C.
W_{MT} = weight of metal tube.
$C_{H_2O \text{ at } 60°C.}$ = sp. ht. of water at 60°C.
W_{H_2O} = weight of water.
T = final temp. of calorimeter system.
t = initial temp. of calorimeter system.

The rise in temperature due to the metal alone, however, is known, and a temperature correction may be made to compensate for this rise. Formula (1) then becomes

$$C_{H_2O \text{ at } 60°C.} W_{H_2O(60-T)} = CW(T - t). \quad (2)$$

The specific heat of the system was calculated by both methods after a series of runs and was determined as 13,847 cal. per °C., which is the value used in making the specific-heat determinations.

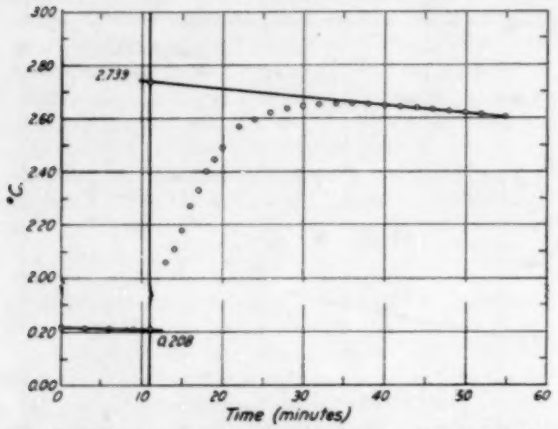

FIG. 7.—Time-temperature correction curve; metal tube plus H_2O at 60°C. inserted in CCl_4; determination No. 1.

Approximately 34 liters (53,890 gm.) of carbon tetrachloride were stirred in the calorimeter, and temperature readings on the Beckmann thermometer were taken every minute until the rate of change in temperature was constant for 10 minutes. The counterbalanced door of the furnace was quickly raised and the wooden plug in the lid of the calorimeter was removed. Using casserole tongs, the jaws of which were at approximately the temperature of the furnace, the casserole was removed from the furnace, the test sample was discharged from the casserole into the calorimeter, and the wooden plug was inserted in the lid of the calorimeter. The time required to transfer the test sample from the furnace to the calorimeter was approximately 5 to 6 seconds. With continual stirring, the rise in temperature of the calorimeter system was noted at one-minute

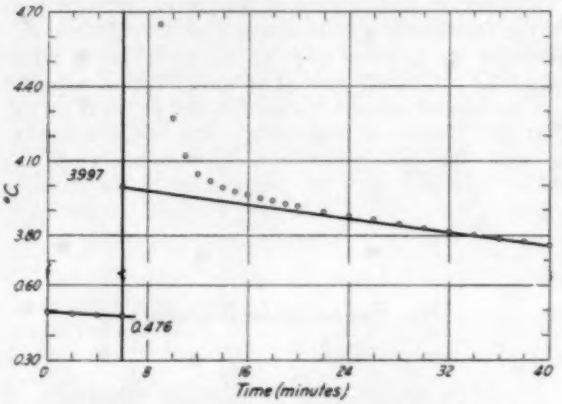

FIG. 8.—Time-temperature correction curve; chrome ore No. 2, fired to cone 32; determination No. 3.

(3) Determination of Mean Specific Heats

Each test sample, consisting of through 8- and on 12-mesh material (prepared as described in section III), was heated in a refractory casserole in the electric furnace to a constant temperature in the vicinity of 850°C. This constant temperature was attained within the electric furnace and the test sample by allowing them to come to equilibrium overnight during a period of 16 hours at a specific setting of the electric furnace rheostat.

TABLE III

COLLECTED AND CALCULATED DATA

Determination No.	Material	Sample wt. (gm.)	Temp. (°C.)	Final bath temp. (°C.)	Initial bath temp. (°C.)	Total rise in bath temp. (°C.)	Mean specific heat between 25° and 850°C. (calculated, cal./gm./°C.)	
1		257.1805	827.5	27.961	24.482	3.479	0.234	
2	Chrome ore No. 1	252.0645	840.9	28.133	24.655	3.478	0.235	0.235
3	(cone 16)	252.5346	832.2	27.893	24.439	3.454	0.234	
4		249.9688	851.3	28.503	25.018	3.485	0.235	
1		252.8554	827.8	28.135	24.704	3.431	0.235	
2	Chrome ore No. 1	259.9560	819.5	29.088	25.579	3.509	0.237	0.236
3	(cone 18)	259.8466	841.0	28.117	24.508	3.609	0.237	
4		252.3138	853.2	28.265	24.720	3.545	0.236	
1		255.4430	853.2	27.920	24.493	3.427	0.225	
2	Chrome ore No. 2	259.5554	837.3	27.736	24.335	3.401	0.224	0.225
3	(cone 32)	261.5330	852.6	28.287	24.766	3.521	0.226	
4		260.2395	850.8	28.815	25.350	3.465	0.224	
1		260.3509	838.6	27.867	24.405	3.462	0.227	
2	Chrome ore No. 2	259.7815	856.3	28.188	24.699	3.489	0.225	0.226
3	(cone 34)	260.0452	846.9	27.879	24.367	3.512	0.228	
4		260.3294	860.9	28.902	25.386	3.516	0.225	
1		260.0190	846.9	29.096	24.728	4.368	0.284	
2	Magnesite ore	260.2821	853.5	29.419	25.051	4.368	0.282	0.283
3	(cone 26)	259.9398	870.5	29.150	24.695	4.455	0.282	
4		260.0917	845.5	29.657	25.326	4.331	0.283	
1		260.1875	856.1	29.346	24.980	4.366	0.281	
2	Magnesite ore	260.0680	843.0	29.134	24.753	4.381	0.287	0.283
3	(cone 28)	259.8749	862.6	28.896	24.506	4.390	0.281	
4		260.2782	846.5	28.637	24.285	4.352	0.283	

intervals over a suitable rating period. The time-temperature curve was plotted, as shown in Fig. 8, which is typical of all the curves obtained. Applying the required cooling correction, the rise in temperature of the calorimeter system was determined and the specific heat of the test sample was calculated.

VI. Test Results

Four determinations were made on each of the samples, and the data obtained in each are given in Table III. The specific heat in each case was calculated in accordance with the following formula:

$$C_S W_S(T_S - T) = CW(T - t).$$

Wherein C_S = mean sp. ht. of sample between T_S and T.
W_S = weight of sample.
CW = heat capacity of calorimeter.
T_S = temp. of sample.
T = final calorimeter temp.
t = initial calorimeter temp.

The results of other investigators, working with chrome ores and chrome brick, pure or relatively pure magnesium oxide, and commercial magnesite brick, are listed for comparison in Table IV.

TABLE IV

COMPARISON OF RESULTS OF INVESTIGATORS

Reference	Material		Temperature (°C.)	Mean specific heat
Regnault[1]	Pure MgO		24–100	0.244
Russel[2]	" "		0–25	0.239
Magnus[3]	" "		22–99	0.234
			15–268	0.252
			15–559	0.267
			16–765	0.276
Steger[5]	98% MgO		25–205	0.246
			25–405	0.264
Steger[6]	Calcined magnesite (84.5% MgO)		0–206	0.225
Heyn, Bauer, and Wetzel[4,7]	Commercial magnesite brick		25–400	0.258
	Analysis (%)			
	SiO_2	0.20	25–605	0.267
	Al_2O_3	0.17	25–825	0.277
	Fe_2O_3	9.31	25–930	0.281
	CaO	0.35	25–1040	0.295
	MgO	88.85	25–1115	0.289
Tadokoro[8,12]	Commercial magnesite brick			
	Analysis (%)			
	SiO_2	18.26	25–200	0.220
	Al_2O_3	0.56	25–400	0.256
	Fe_2O_3	0.80	25–605	0.266
	CaO	Trace	25–825	0.264
	MgO	76.43	25–930	0.264
	Commercial chrome brick		30–218	0.178
	Analysis (%)			
			30–313	0.195
	SiO_2	21.80	30–382	0.210
	Al_2O_3	30.10	30–480	0.216
	Fe_2O_3	13.67	30–579	0.221
	MgO	12.47	30–687	0.219
	Cr_2O_3	19.47	30–796	0.218
			30–894	0.215
Green[9]	Commercial magnesite brick		25–605	0.265
	Analysis (%)			
			25–825	0.274
	SiO_2	2.34	25–930	0.280
	Al_2O_3	No data	25–1040	0.285
	Fe_2O_3	2.56	25–1115	0.292
	CaO	4.68		
	MgO	87.88		
G. B. Wilkes[10]			30–100	0.2335
			30–300	0.2470
			30–500	0.2590
			30–700	0.2690
			30–900	0.2765
	U.S.P. MgO, calcined at 1800°C.		30–1100	0.2825
			30–1300	0.2875
			30–1500	0.2910
			30–1700	0.2935
			30–1800	0.2945

VII. Summary and Conclusions

(1) The mean specific heats of the materials, which were described in Table II, are as follows:

Material	Cone	Mean specific heat (25°–850°C.)
Chrome ore No. 1	16	0.235
" " " "	18	0.236
" " No. 2	32	0.225
" " " "	34	0.226
Magnesite ore	26	0.283
" "	28	0.283

(2) In each of the chrome ores, the higher fired ore had the higher mean specific heat. This follows the van't Hoff-Thompson law, according to which that modification of a body which is stable at a high temperature has a higher mean specific heat than the modification of the same body which is stable at a lower temperature.

(3) Chrome ore No. 1 has slightly higher mean specific heat than chrome ore No. 2 to which magnesite has been added; the magnesite added, however, has a much higher mean specific heat than either one.

(4) The figures reported are applicable to samples of the analyses and characteristics given in the paper when the samples have received the specific treatments described.

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This bibliography is divided into two sections. Section A lists the references mentioned in the article. Section B was prepared to serve as a background for the study prior to carrying out the work described in the paper and is submitted as an aid to other workers in this field.

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June, 1941

20—6

Abrasives

Abrasive cutting-off machine. Anon. *Automobile Engr.*, **30** [402] 301 (1941).—A recently developed abrasive cutting-off machine with a wheel spindle speed of 4000 r.p.m. is described. M.B.H.

Abrasive wheels and modern grinding. W. R. Gutteridge. *Jour. Record Trans. Junior Inst. Engrs.*, **49**, 481 (1938–39).—G. discusses the manufacture of alumina and silicon carbide abrasive wheels using such bonding agents as resinoid or Bakelite, rubber, shellac, sodium silicate, or a vitrified type. B.C.R.

Conception, development, equipment, and measuring methods of an entirely new surface finish method—superfinish. William F. Sherman. *Iron Age*, **142** [Sept. 1] 18–23; [Sept. 8] 40–45; [Sept. 22] 57–61, 90 (1938); *Metals & Alloys*, **10** [1] MA42 (1939).—S. describes a new surface finish produced upon flat, internal, external, round, and other types of surfaces by a combination of short motions, light abrasive pressures, slow abrasive cutting speeds, hard abrasive stones, and a lubricant of proper viscosity that eliminates scratches and surface defects created by previous mechanical operations without creating scratches or defects. He also presents new conceptions and definitions of terms used and compares the use of this technique with conventional methods of finishing automotive parts. Measurement of temperatures on metal surfaces, hardness, ductility, and strength of oil films and other lubricant specifications which must be taken into account with this process are dealt with.

Fifty years of abrasive manufacturing. Anon. *Mfrs. Record*, **110** [3] 20 (1941).—The history of abrasive manufacturing and the uses of silicon carbide abrasives are discussed. B.C.R.

Mechanical polishing with a film of abrasive. J. Osborne Fuller. *Econ. Geol.*, **36** [2] 199 (1941).—F. discusses an improved polishing method utilizing a film of abrasive on a metal lap, which provides a greater number of active cutting particles than does a fixed abrasive. A mounted specimen may be ground and polished in less than 1 hr. A detailed description of the procedure is given. B.C.R.

Strip grinder. Anon. *Iron Age*, **142** [Dec. 8] 41 (1938); *Jour. Iron & Steel Inst.* [London], **139** [1] 158A (1939).—An electrically driven grinding and polishing machine for use on steel strip up to 30 in. wide and down to 0.005 in. thick is fitted with an automatic compressed-air control for the belt alignment and an automatic control by which the pressure on the grinding or polishing belt can be set and maintained constant. This machine is intended to condition stock strip which cannot be rolled out because of surface imperfections, to improve cold-rolled finishes, and to produce a finely ground surface to match standard sheet finishes.

Structural changes in the surface layers of hardened steel under the influence of polishing. L. V. Altshuler and M. P. Speranskaya. *Vestnik Metalloprom.*, **20** [1] 15–21 (1940).—Austenite appears on the surface of samples of hardened steel under the influence of polishing to a great depth with coarse grains. A large number of steel samples showed the transition of martensite into austenite during mechanical working by polishing. During polishing the following structural changes take place: (1) the surface layers contain more austenite, (2) the quantity of austenite formed by polishing increases with the temperature of hardening, (3) the polishing of nonhardened steel does not cause the appearance of austenite, and (4) austenite is formed whether or not the metal is cooled during polishing. B.E.K.

Substitute for diamonds used in industry. Franz Urbanek. *Schleif- & Poliertech.*, **17**, 99–101 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 1491.—Diamonds and diamond abrasive disks, small steel wheels for cutting, saws for rock, boron carbide as abrasive, and truing diamonds are discussed. M.V.C.

Vertical oscillatory grinder. Anon. *Automobile Engr.*, **30** [404] 371–72 (1941).—A new machine for grinding tools to a high degree of precision is described. The diamond wheel dresser is fastened to the table top and can be moved by means of screw and slide. The adjustable slide provides for large or small grinding wheels; a form wheel may be used. M.B.H.

PATENTS

Abrading machines. NORTON CO. Brit. 533,972, March 12, 1941 (Oct. 3, 1938).

Abrading wheel. F. F. HILLIX (American Steel and Wire Co.). U. S. 2,236,709, April 1, 1941 (Sept. 9, 1938).

Apparatus for cracking and handling glass sheets. H. C. SHOCK (Libbey-Owens-Ford Glass Co.). U. S. 2,236,011, March 25, 1941 (Jan. 18, 1939).

Apparatus for dressing or forming grinding wheels used for grinding or finishing gear teeth. J. E. WAINWRIGHT (Coventry Gauge & Tool Co., Ltd.). U. S. 2,237,975, April 8, 1941 (July 11, 1940).

Apparatus for forming or dressing grinding wheels for use in form-grinding operations. J. E. WAINWRIGHT (Coventry Gauge & Tool Co., Ltd.). U. S. 2,237,976, April 8, 1941 (July 11, 1940).

Apparatus for forming or dressing the operative surface of grinding wheels. J. E. WAINWRIGHT. U. S. 2,237,977, April 8, 1941 (Sept. 3, 1940).

Apparatus for grinding lenses. R. F. METZGER. U. S. 2,236,713, April 1, 1941 (Aug. 4, 1938). U. S. 2,236,714, April 1, 1941 (Aug. 4, 1938; Dec. 14, 1940).

Cutter grinding method. C. E. KRAUS (Ingersoll Milling Machine Co.). U. S. 2,238,064, April 15, 1941 (May 16, 1938).

Grinding machine. G. T. MUSKOVIN (Norton Co.). U. S. 2,237,496, April 8, 1941 (May 23, 1940). A. RENFREW. Brit. 534,234, March 12, 1941 (Aug. 31, 1939).

Grinding wheel. EDWARD VAN DER PYL (Norton Co.). U. S. 2,238,351, April 15, 1941 (Dec. 24, 1940).—An abrasive article comprises diamonds bonded with a hard, friable, sintered metal bond capable of being sintered at between 600° and 850°C.

Grinding wheel spindle reciprocating apparatus. C. C. ALVORD (Norton Co.). U. S. 2,237,467, April 8, 1941 (June 8, 1939).

Honing device. H. S. INDGE (Norton Co.). U. S. 2,238,326, April 15, 1941 (Nov. 26, 1938).

Honing or sharpening device for cloth-cutting machines. JACOB SILBERSTANG. U. S. 2,236,038, March 25, 1941 (Aug. 5, 1938).

Hydraulic system for machine tools, etc. W. J. GUILD (Heald Machine Co.). U. S. 2,238,110, April 15, 1941 (May 5, 1937).

Industrial diamond wheel. J. H. L. DE BATS (Metal Carbides Corp.). U. S. 2,216,908, Oct. 8, 1940 (July 16, 1936).—A diamond surfaced dressing wheel has a surface of particulate diamonds embedded in a forged carbide mixture comprising 90 to 95% tungsten carbide and 10 to 5% chromium carbide.

Lapping apparatus. D. A. WALLACE (Chrysler Corp.). U. S. 2,238,760, April 15, 1941 (July 22, 1936; Aug. 1, 1938).

Lapping machine. H. S. INDGE (Norton Co.). U. S. 2,238,646, April 15, 1941 (Sept. 25, 1940). U. S. 2,238,859, April 15, 1941 (Sept. 15, 1939).

Locomotive and car wheel grinding machine. R. G. MCGOWAN. U. S. 2,236,438, March 25, 1941 (Jan. 4, 1940).

Means for assembling elements of a buffing wheel. E. W. HALL. U. S. 2,236,901, April 1, 1941 (May 5, 1937; Oct. 9, 1937).

Means for forming grinding wheels for use in grinding internal screw threads. J. E. WAINWRIGHT (Coventry Gauge & Tool Co., Ltd.). U. S. 2,237,974, April 8, 1941 (Nov. 14, 1939).

Metallic blasting and abrasive material. O. E. HARDER (Globe Steel Abrasive Co.). U. S. 2,218,107, Oct. 15, 1940 (Dec. 7, 1939).—Metallic blasting and abrasive material formed of chilled iron base particles containing at least 0.2% copper as an alloying element, the material having a hardness of at least 550 Brinell.

Motor-driven grinding or abrading machines. T. S. HARRISON & SONS, LTD., AND E. C. ASHTON. Brit. 533,864, March 5, 1941 (Dec. 6, 1939).

Polishing material and method of manufacturing. OTIS HUTCHINS (Carborundum Co.). U. S. 2,235,880, March 25, 1941 (April 6, 1939).—A method of making polishing material comprises calcining bauxite and grinding the calcined bauxite in the presence of water to increase the absorptive power of the bauxite particles for an organic binder.

Polishing and wet sanding. J. N. BAKER AND G. C. WILHIDE (Black & Decker Mfg. Co.). U. S. 2,238,096, April 15, 1941 (Aug. 16, 1939).

Rubber-base sheeted abrasive. L. A. HATCH (Minnesota Mining & Mfg. Co.). U. S. 2,236,597, April 1, 1941 (Nov. 10, 1928; Sept. 28, 1933).

Self-cooling buffing wheel. C. J. PETERSON AND A. H. PETERSON. U. S. 2,236,444, March 25, 1941 (Oct. 18, 1940).

Surface-finishing machine for cylindrical surfaces. D. A. WALLACE (Chrysler Corp.). U. S. 2,238,761, April 15, 1941 (May 22, 1939).

Surface-grinding machine. P. V. MILLER (Taft-Peirce Mfg. Co.). U. S. 2,238,704, April 15, 1941 (Nov. 3, 1939).

Titanium carbide and method of making. R. R. RIDGWAY (Norton Co.). U. S. 2,237,503, April 8, 1941 (April 19, 1937).—(1) A composition of matter comprises a massive ingot of titanium carbide having a hexagonal columnar crystalline structure with the majority of the individual crystals larger than 100-grit size and characterized by a high metallic luster and well-defined crystal faces and sharp edges, a hardness above 9 on Mohs' scale, and a density greater than 4.75, which is substantially free from titanium nitrogen compounds as well as iron, silicon, graphite, and alkaline-earth metals. (2) A method of making titanium carbide comprises the steps of completely fusing titanium oxide and thereafter cooling and crystallizing it, mixing the crystalline product in a granular condition with carbon proportioned stoichiometrically for making titanium carbide, heating the mixture about a furnace resistor while excluding oxygen and nitrogen, and progressively forming an ingot of titanium carbide therefrom.

Tool for use in grinding the valves of internal-combustion engines. J. S. HOLTON. Brit. 534,203, March 12, 1941 (Jan. 19, 1940).

Art and Archeology

Best of Ming in rare full view. JOHN POPE. *Art News*, **39** [14] 7–8 (1941).—P. describes the porcelains from the Samuel C. Davis collection just installed at Harvard's Fogg Museum and tells much of general interest regarding the Ming period (A.D. 1368–1644), in which the manufacture of porcelain reached its technical peak and the potter and the decorator had complete mastery of their arts. This collection includes many pieces of underglaze blue decoration combined with brilliant low-fired enamels over the glaze; in this respect it is unique in this country. Representative examples show (1) from the Ch'êng Hua period (A.D. 1465–1487), the delicate lines and pale coloring of the *tou-ts'ai* enamel decoration; (2) from the Ch'êng Tê period (A.D. 1506–1521), the use of Ming yellow with underglaze blue floral patterns; (3) from the Chia Ching period (A.D. 1522–1566), the strong hues of the *wu-ts'ai* enamel technique; and (4) from the Wan Li period (A.D. 1573–1619), the combination of rich underglaze blue with brilliant *wu-ts'ai* enamels. Illustrated. M.E.P.

Peter Carslegh's window in Winscombe Church, Somerset. C. WOODFORDE. *Jour. Brit. Soc. Master Glass Painters*, **8**, 51–57 (1939–1940).—A description of the west window of the chancel of Winscombe Church and a brief biography of Peter Carslegh who presented the window are given. The window shows the natural culmination of the use of yellow stain which is of an unpleasantly hot orange

tone. It gives the impression of being the work of men striving not very successfully to keep abreast of the times. Illustrated. M.B.H.

Ceramic colors. ANON. *Ceram. Ind.*, **35** [4] 87–110 (1940).—A detailed compilation is presented, with formulas, of methods of producing in glass, enamel, and pottery bodies and glazes various shades of black, blue, brown, green, metallics, orange, red, violet, and yellow. A.F.M.

Control of iron oxide in volcanic ash. E. D. KINNEY. *Bull. Amer. Ceram. Soc.*, **20** [4] 118–21 (1941).—1 reference, 1 figure.

Denmark excavates in Syria. HARALD INGHOLT. *Asia*, **41**, 199–204 (1941).—An old citadel mound near Hama was excavated. Twelve layers, A to M (I omitted), were found, but levels A to D are of historic times and are not described. Level M has brown or black pottery, sometimes burnished, and dates from the fifth millenium B.C. Level L, dating from about 3500–3000 B.C., has a typical pottery with painted geometric designs; there is also a figurine and a terra-cotta seal. Large funerary jars are found in level K (3000–2500 B.C.), together with burnished pottery, red or yellow polished pottery, a faience seal cylinder, and some bronze tools. Level J (2400–2000 B.C.) has gray or black goblets with spiral painted designs and many figurines. Level H (1950–1750 B.C.) is characterized by a carinated bowl engraved in lines, points, and notches. Other pottery objects include a hollow cylindrical column, used as a brazier, and many figurines. Level G (1550–1450 B.C.) has gray pottery of elegant form, a Cypriote "milk bowl," and the so-called Nuzi ware. Of level F little has been preserved other than many cinerary urns below the mound. A little iron was found. This level lasted until about 950 to 900 B.C. The Semites then replaced Indo-Europeans. The most extensive remains belong to level E, when the city was at the height of its power. Many large buildings were found. This level ended with the capture and destruction of the city by Sargon. W.D.F.

Earlier than Ming in the Davis St. Louis bequest. ANON. *Art News*, **39** [14] 8 (1941).—With the addition of part of the Samuel C. Davis collection of Chinese ceramics, the St. Louis City Art Museum's collection has become one of the most important in this field because of the quality and inclusiveness of the individual pieces. Representative pieces are described. Illustrated. M.E.P.

Examination of a Chinese temmoku glaze and body. W. H. EARHART. *Bull. Amer. Ceram. Soc.*, **20** [4] 121–22 (1941).—2 figures.

Glazed windows of Moreton Old Hall, Cheshire. W. J. PEARCE. *Jour. Brit. Soc. Master Glass Painters*, **8**, 68–75 (1939–1940).—All of the windows of the Hall have been filled with patterned glazing, and although they date from 1559–1580 they are in fairly good condition. The old glass is unbleached white, mostly small sheets made from cylinders cut and opened out. The unbleached glasses have tints of green, yellow, and faint purple due to slight metallic impurities, probably copper, iron, and manganese. The original glass is very thin and brilliant on the fire surface and in places slightly iridescent. The cutting was probably done by the glazing iron, no evidence being found of a diamond cut. No cementing had been done; the leads were cleanly pressed down and a fluid oil or varnish which had no body or substance was brushed in. Illustrated. M.B.H.

It can happen here. RAYMOND G. GIBNEY. *Ceram. Ind.*, **36** [2] 40–46 (1941).—G. reports on the exhibitions, business, attendance, and trends in design at the 61st annual Pittsburgh pottery and glass show, Jan., 1941. Illustrated. A.F.M.

Walter Jodok Kohler. ANON. *Bull. Amer. Ceram. Soc.*, **20** [4] 134–37 (1941).

Living kitchen permanent exhibit at Syracuse Museum of Fine Arts. ANON. *Bull. Amer. Ceram. Soc.*, **20** [4] 149–50 (1941).—2 photographs.

Majolica plate by the Maestro Giorgio. HELEN COMSTOCK. *Connoisseur*, **106** [472] 256–57 (1941).—A recent addition at the Toledo Museum of Art is a majolica plate, an example of the work of Giorgio Andreoli of Gubbio, dated 1531 and signed with the initials M. G. The plate is 9½ in. in diameter and is decorated in the center with the profile of a young woman and on the border with *grottesche* and arabesques. The coloring combines blues and gray-brown, over which is the ruby-red iridescent glaze for which Gubbio was famous. The Maestro Giorgio, one of a family distinguished at Gubbio, used the ruby luster and an inimitable golden yellow in a manner which made his name famous. Other artists often sent their work to him for the final addition of luster. Illustrated. M.E.P.

Manufacture of leadless glazes for face tile of the Khalturin plant. E. KLIBINSKAYA. *Keram. Sbornik*, **1939**, No. 1 (2), pp. 52–53.—The composition and behavior of various glazes without lead were studied. The results are tabulated. Such glazes must possess a high elasticity, gloss, low firing temperature, and wide fusing interval. M.V.C.

Matchless Ming vases a gift to Kansas City. ANON. *Art News*, **40** [2] 35 (1941).—The William Rockhill Nelson Gallery's new acquisition is a pair of blue and white Chinese baluster-shaped vases from the period of Emperor Hsüan Teh. They are 21 in. high and painted with a dragon design; the thick, blue-white glaze shows the prized "orange skin" texture. The vases constitute a true pair with the design reversed. See "Ming. . . ," *Ceram. Abs.*, **20** [5] 111 (1941). M.E.P.

Medieval painted glass of Teynham (Kent). C. R. COUNCER. *Jour. Brit. Soc. Master Glass Painters*, **8**, 63–67 (1939–1940).—C. describes the old glass still remaining in the church, most of which is now collected in two windows in the north transept. Most of the glass dates from the 15th century and is of good workmanship. M.B.H.

Releading and rearrangement of ancient glass in Bale Church, Norfolk. D. KING. *Jour. Brit. Soc. Master Glass Painters*, **8**, 58–62 (1939–1940).—The east window in the south aisle of Bale Church, containing a mixture of 14th- and 15th-century work, was completely releaded and rearranged in 1938. The whole window consisted of about 2000 pieces, and a description is given of the glass as it now appears. The drawing and composition are exceptionally good; it is an example of Norwich glass painting at its best. Illustrated. M.B.H.

Ruin sites in Turkistan. ERNST COHN-WEINER. *Asia*, **41**, 102–108 (1941).—This section is one of the most rewarding in a study of Islamic and pre-Islamic art. Samarkand has many monuments with faience mosaics and many important ruins. In the Greek period, terra-cotta medallions of heads were used to decorate even common pottery. There are also terra-cotta human figures, 4 to 5 in. high, in large quantities and varieties. In Islamic times, splash glazed ware was made, together with ware decorated with pomegranates, etc. Under the Karakhanids, inscriptional friezes became the prominent ceramic decoration. Other types include a rare black clayware with white decorations. At Uzkend are well decorated mausoleums, and at Safed Buland is a tomb tower with beautiful stucco decoration. Other important localities are Merv, Sultan Kala, and Bokhara. W.D.F.

Stained glass: its background and foreground. H. W. RAMBUSCH. *Glass Ind.*, **22** [3] 122, 125 (1941).—Ceramic glazes and stained glass are compared. The stained-glass craft has used colored glass with trace lines and lead strips, silver-stained glass, colored enamels, opalescent glass, and glass blocks. A new orientation is taking place for adjustment to modern developments. The Mapparium in the Christian Science Publishing Society building in Boston illustrates this new trend. A.P.

Substitutes in the manufacture of coloring materials and glazes for ceramic art products. ANON. *Keram. Rundschau*, **48** [8] 63–65; [11] 96–98 (1940).—Due to the scarceness (in Germany) of many raw materials which were formerly used in the manufacture of majolica, tile, etc., e.g., tin oxide, red lead, manganese, and rutile, substitutes are employed which, if properly applied, give warm tones and color effects comparable to those of prod-

ucts of the 16th and 17th centuries. The clays to be used, their treatment, and the additions of fluorspar, magnesite, potash, or soda are described. For daily utensils the colored clay must be dense and smooth after firing; a suitable composition is 100 parts by weight of fat yellow-red firing clay, 5 Meissen clay, 2.5 barium carbonate, 8 iron oxide, 12.5 Oasin manganese, 1 cobalt oxide, 12 magnesite, 3 fluorspar, and 10 sintering powder; it is fired at Seger cone 02*a*. The surface becomes smooth and velvety. Water absorption is 3% maximum. The brown color of earthenware is produced by the Oasin manganese together with cobalt oxide. As red-firing clays always contain more or less large amounts of alkali, Mg, or Ca sulfate, which often produce white spots, a few percent of barium carbonate should be added to prevent this. A glaze for a body firing at Seger cone 02*a* of the following composition is recommended: 150 parts by weight of lead silicate ($1PbO:1SiO_2$) finely ground, 17.5 annealed kaolin, 7.5 raw kaolin, 25 quartz meal, 1.5 calcite, and 1.5 yellow coloring material. If a glaze is applied only on one side (the inside of vessels), tensions between the body and the glaze must be relieved to avoid cracks in the glaze. Red lead can be replaced by soda, potash, magnesite, pegmatite, or glass powder for high firing temperatures, but for art ceramics of Seger cones 07*a* to 02*a* no substitute has been found; Pb silicates can be used. Substitutes include, for tin oxide, Terrar Nos. 500 and 600, cerium oxide Opaline No. 29,650, and Stannit, and, for rutile, titanium dioxide, Kronos titanium dioxide S 1053, Kronos titanium specialty S 1161, and ivory body 23,169 Lffa. Mn can be replaced by Oasin Mn. Experiments with these substitutes which did not always give satisfactory results are described. A black glaze was found to be satisfactory if composed of 35 parts Pb silicate, 6 kaolin, 7.5 Terrar No. 600, 1 ivory body, 0.5 chalk, 2 dark brown metallic frit, 1.5 dark blue coloring material, 0.5 cobalt oxide, and 1 Cu oxide. In an ivory glaze, the substitutes often changed the colors, light yellow changing to dark orange, light blue to dirty blue, deep blue-green to light green, and reddish brown to coffee brown. M.H.

Terra sigillata glazes. M. DÉRIBÉRÉ. *Rev. Matériaux Construction Trav. Publics*, No. 357, pp. 61–62B (1939).—The materials comprising the brilliant red glaze of the antique terra sigillata have been found to be red clay, pumice stone, and potash (*Ceram. Abs.*, **13** [4] 79 (1934)). The excellence of the glazes made by the Romans and Gallo-Romans testifies to their mastery and skill in ceramic art. The making of red pottery in the Roman province of Gaul (France) was learned from the Romans, and some of the raw materials were perhaps brought in from Italy. M.V.C.

Wah—late of Thebes, Egypt. H. E. WINLOCK. *Sci. Amer.*, **164**, 150–52 (1941).—This mummy was discovered in 1920 but was not unwrapped until recent X-ray examination showed much jewelry on it, including several strings of faience beads and others of precious metals and semiprecious stones, a faience scarab, and a high collar, bracelets, and anklets of greenish blue beads. W.D.F.

Robert A. Weaver presents European enamels to the Cleveland Museum of Art. WILLIAM M. MILLIKEN. *Bull. Cleveland Mus. Art*, No. 10 (Dec., 1940); reprinted in *Bull. Amer. Ceram. Soc.*, **20** [4] 147–48 (1941).—1 reference, 1 photograph.

Winning America for American ceramics. ANON. *Ceram. Ind.*, **35** [5] 28–36; [6] 34–37 (1940).—Steps being taken by American manufacturers of dinnerware, glassware, and art pottery to create distinctive American designs and to take permanent advantage of the cessation of war-interrupted imports are discussed. The following short articles are included: **American industry has able ceramic artists.** JOHN N. FRANK. *Ibid.*, [5] 32–33. **American ceramics equal ware formerly imported.** CHARLES L. GAUNT. *Ibid.*, [5] 33. **Develop self-sufficiency in American ceramic industry.** FAYE G. BENNISON. *Ibid.*, [5] 34–35. **New ceramic developments occur only in United States.** FREDERICK H. RHEAD. *Ibid.*, [5] 35–36. **Develop ceramic types suitable to American conditions.** FREDERICK H. RHEAD. *Ibid.*, [6] 35–36. **Will the American buyer play ball with manufacturers?** VIKTOR SCHRECKENGOST. *Ibid.*, [6] 36–37. Illustrated. A.F.M.

BOOKS

Country Craft Book. On Working with Wood, Clay, Metals, Stone, and Color, with Many New Recipes and Secrets of the Crafts Now First Published. RANDOLPH WARDELL JOHNSTON. Countryman Press, Inc., Weston, Vt.; Farrar & Rinehart, Inc., New York, 1937. 200 pp., 35 figures including wood engravings.—The section on working with clay comprises 55 pp. of highly condensed directions on finding and preparing clays; making pottery, tile, and glazes; building kilns, wheels, and ball mills out of available scraps; and decoration. Four woodcuts illustrate wedging, treading, and two stages of throwing. The universal appeal of clay working and the community joys it inspires are emphasized. The worker who, living in country districts, is cut off from ready access to libraries, museums, and workshops of other craftsmen will find in this book sufficient solid basic information to make a good beginning and to go a long way toward developing his own style without any other help. A.P.

Perachora. Sanctuaries of Hera Akraia and Limenia. Excavations of the British School at Athens, 1930–1933. Architecture, Bronzes, and Terra Cottas. HUMFRY PAYNE ET AL. Oxford University Press, Clarendon Press, Humphrey Milford, London. Price 84s. Reviewed in *Times Lit. Supp.*, **39** [2030] 651 (1940).—This is the first full report of the work carried out at Perachora. The chief archeological interest centers in the temples, and comparison of the finds, particularly in bronze and pottery, shows how the geometric Hellenic world was influenced by the new materials and ideas which were opened to it, both from the east and the west, in the second half of the 8th century B.C. The clay temple models and some fine terra cottas are also of great interest. The book contains full maps and plans and 140 plates; it is a record of one of the major British archeological achievements of the century. K.W.W.B.

Prehistoric England. GRAHAME CLARK. B. T. Batsford, Ltd., London. Price 8s 6d. Reviewed in *Times Lit. Supp.*, **40** [2032] 14 (1941).—C. presents an account of England and its inhabitants from Neolithic to Roman times. It is primarily of interest to the general reader but contains some references to pottery, stone, and metal work. Illustrated. K.W.W.B.

Rajagriha in Ancient Literature. B. C. LAW. Archeological Survey of India. Reviewed in *Current Sci.*, **8** [2] 92 (1939).—Rajagriha, still known as Rajgir, is easily identified by the configuration of the hills by which it is surrounded, the other name of the town being *Girivraja*, or mountain fastness. One of the most wonderful cities of ancient India, it goes back to the days of the Buddha and continues to be a place of pilgrimage and a health resort. Modern excavations have been particularly fruitful at Rajgir, and there is ample scope for research at this ancient historical city. Details are given of the various names by which the ancient city of Rajagriha was known and their significance, together with the topography of the various sites in and around the city and of the hot springs, the bamboo forest, the mango grove of Jivaka, the Sattapanni cave, and other places associated with incidents in the life of the Buddha and the history of Buddhism. The importance of Rajagriha in the religious and cultural history of India is brought out, and recent discoveries of the Archeological Department show that, from the earliest times, Rajagriha was a notable center of Naga worship. A.P.S.

PATENTS

Designs for:

Bathtub. C. H. WIDMAN (Murray Corp. of America). U. S. 126,676 and 126,677, April 15, 1941 (Oct. 5, 1939).
Bottle. FYON & FYON, LTD. Can. 12,975, Feb. 15, 1941. G.M.H.

Bottle. W. J. LUNDY (Olean Glass Co.). U. S. 126,209, April 1, 1941 (Jan. 10, 1941).

Chinaware and earthenware. DOULTON & Co., LTD. Can. 12,983, March 12, 1941. G.M.H.

Glass bank. F. S. BARBIERS (Anchor Hocking Glass Corp.). U. S. 126,549, April 15, 1941 (Jan. 3, 1941).

Goblet. A. J. CUNNINGHAM. U. S. 126,360 to 126,363, April 8, 1941 (Feb. 7, 1941). U. S. 126,364 and 126,365, April 8, 1941 (Feb. 18, 1941).

Spark plug. B. H. SIBLEY (Champion Spark Plug Co.). U. S. 126,466 and 126,467, April 8, 1941 (May 10, 1940).

Ornamentation of ceramic ware. W. H. EARHART (Harshaw Chemical Co.). U. S. 2,238,018, April 8, 1941 (Dec. 9, 1938).—A process of ornamenting glazed ceramic ware comprises applying thereto a size having the property of drying to a tacky state and upon further drying becoming inert to essential oils, the size consisting essentially of an alkyd resin, a cellulose resin of the class consisting of cellulose nitrate, cellulose acetate, and ethyl and benzyl celluloses, a minor amount of an organic plasticizer in which the resins are soluble, and a solvent for the composition, drying to a tacky state, applying decalcomania decoration, drying beyond the tacky state, washing off the backing of the decalcomania, applying a decoration at least a part of which overlies the size and which is carried by an essential oil vehicle, and thereafter firing the ware.

Cements

Microscopic investigation of cement clinker. K. OBENAUER. *Mikrokosmos*, **33**, 161–65 (1939–1940); *Chem. Abs.*, **35**, 1596 (1941).—Polished and water-etched surfaces are examined by means of incident light to estimate the relative amounts of $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, and Ca aluminates present. Pulverized cement mixed with a binder such as sealing wax can be studied by the same technique. $3CaO \cdot SiO_2$ is easily identified, chiefly as hexagonal-shaped crystals. More intense etching with water reveals $2CaO \cdot SiO_2$ as oval-shaped forms in the ground mass and as lamellar inclusions in $3CaO \cdot SiO_2$. The differentiation of $3CaO \cdot Al_2O_3$, $13CaO \cdot 7Al_2O_3$, and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is very difficult. O. suggests that these minerals can be identified by the simultaneous use of transmitted and incident light on a surface-polished thin section.

Properties of Portland cement and methods of determining them. GABRIEL A. ASHKENAZI. *Cement & Lime Manuf.*, **11**, 119–25 (1938); *Chem. Abs.*, **32**, 6827 (1938).—A brief account is given of the methods of examination used at present and their efficiency in the estimation of the properties of Portland cement. The most important and generally used methods are far from perfect because of the complicated nature of cement as well as the lack of a clear conception of concrete. The experimental work carried out during the last decade has greatly extended the knowledge, but it is still of somewhat fragmentary character and cannot be linked into a coherent theory.

Raw-mix synthesis from the raw materials of Portland cement. H. HEIN. *Zement*, **29** [9] 97–100; [10] 113–18 (1940).—H. develops a method (based on the formula of Lea and Parker, "Quaternary . . .," *Ceram. Abs.*, **15** [1] 7 (1936)) of determining the Portland cement raw mix by introducing the new terms of "available" CaO, SiO_2, and Al_2O_3 which indicate those quantities of CaO, SiO_2, and Al_2O_3 that remain after the chemical requirements of the raw mix have been satisfied. Examples and a graphical interpretation are given. F.E.S.

PATENTS

Art of preparing cement products. J. A. SOURWINE. U. S. 2,238,540, April 15, 1941 (July 3, 1940).—A new cement product formed by combining through mixing and compacting and curing dry powdered cement with a non-aqueous organic indurating liquid, which as a generic group includes liquid aromatic hydrocarbons, liquid alcohols, and mixtures of the liquids, to form a hard firm cement matrix.

Thermal insulating cement. J. R. MUSGRAVE (Eagle-Picher Lead Co.). U. S. 2,237,745, April 8, 1941 (April 6, 1939).—A thermal insulating cement comprises a substantially neutral mineral wool, asbestos, bentonite, trisodium phosphate, and sodium nitrite.

Enamel

Acid-resistant enamels for steel constructions. A. M. TRAKHTENBERG. *Khim. Mashinostroenie*, **1940**, No. 7, pp. 18–21; *Chem. Abs.*, **35**, 865 (1941).—On the basis of an investigation of the effects of various components on the acid resistance of enamels for steel constructions the following limits are suggested: SiO_2 56 to 57, Na_2O 15 to 22, K_2O 0 to 8, CaO 0 to 6, TiO_2 0 to 8, Al_2O_3 2 to 4, CaF_2 0 to 3, MgO 0 to 4, B_2O_3 0 to 3, ZrO_2 0 to 4, and ZnO 0 to 4%. The following are suggested because of resistance against HCl, HNO_3, H_2SO_4, various organic acids, and mixtures of organic and mineral acids: (1) SiO_2 61, Na_2O 18, K_2O 5, CaF_2 2.4, CaO 5, TiO_2 5, B_2O_3 1, and Al_2O_3 2.9%; (2) SiO_2 64, Na_2O 17, K_2O 8, CaF_2 2.5, ZnO 2, TiO_2 2, MgO 2, and Al_2O_3 2.5%; (3) SiO_2 58, Na_2O 17, K_2O 8, CaO 2.5, ZnO 2, TiO_2 8, MgO 2, and Al_2O_3 2.5%; (4) SiO_2 58, Na_2O 17, K_2O 8, CaF_2 2.5, ZnO 2, TiO_2 8, MgO 2, and Al_2O_3 2.5%; (5) SiO_2 57.5, Na_2O 16.7, K_2O 7.8, CaF_2 2.5, ZnO 1.96, TiO_2 7.8, MgO 1.96, ZrO_2 1.2, and Al_2O_3 2.4%. The solubilities in 20.24% HCl are 0.31, 0.21, 0.28, 0.30, and 0.21, respectively, and the coefficients of cubic expansion are 337.4, 319.9, 345.7, 339.7, and 335.5 $\times 10^{-7}$, respectively.

Automatic pickler doubles output and improves quality of ware. ANON. *Ceram. Ind.*, **36** [3] 46–48 (1941).—A description is given of the automatic pickler and continuous furnace at the plant of the Florence Stove Co., Kankakee, Ill. The mechanization of pickling operations increases production from 35,000 or 40,000 sq. ft. per day to 75,000 sq. ft. and improves the quality of the ware. The pickling tanks are arranged in two parallel lines about 10 ft. apart. In between and running slightly above the tank level is a continuous side-conveyer chain, on which, at 5-ft. intervals, are attached downward curving cast aluminum conveyer arms. These arms, which carry the ware, are mounted with pivots to allow the raising and the lowering of the ware into the various solution tanks. The transfer of ware from tank to tank is accomplished by a hardened roller mounted on the short end of each carrier arm; these rollers move along a track which includes a number of hump-type cams so that the ware is successively lifted, carried to the next tank, and again immersed. The nickel-dip tank is made recirculating by the attachment of a portable pump-filter apparatus which extracts, filters, and returns 2000 gal. of the nickel solution per hr. Illustrated. A.F.M.

Boron-free soda enamels. H. LANG. *Keram. Rundschau*, **48** [9] 76–79 (1940).—L. gives the following recipes: (1) for a soft white enamel, feldspar 36, quartz 30, soda 30, cryolite 12, fluorspar 7, calcite 3, and saltpeter 2 parts; mill addition, 10 to 12 clay, 6 opacifier, and 1% soda; (2) for a harder white enamel, feldspar 34, quartz 22, soda 22, fluorspar 8, sodium fluosilicate 6, saltpeter 6, and antimony 6; mill addition, 6% clay and 1% soda; (3) for a typical feldspar white, feldspar 64, soda 17, cryolite 12, saltpeter 3, kaolin 4, and antimony 4; mill addition, 8 clay, 5 opacifier, and 1% soda; (4) for the production of most of the color enamels, feldspar 36, quartz 21, soda 26, sodium phosphate 12, glass powder 20, and fluorspar 6;

mill addition (for brown), 8 clay, 6 to 8 iron oxide, and 1% soda; for other colors, iron oxide is replaced by corresponding oxides. A good boron-free glass enamel is as follows: glass powder 52, soda 12, fluorspar 14, kaolin 6, quartz 6, saltpeter 5, and antimony 5. M.H.

Cerium oxide as an opacifying agent is equal to tin or zirconium. ROBERT L. NEWTON. *Ceram. Ind.*, **36** [2] 57–58 (1941).—After reviewing the important literature on the use of cerium oxide in porcelain enamels, N. states that his experiments using this oxide as a frit addition resulted in an increase of the opacity of clear frit enamels but showed little effect in connection with opaque frit enamels with the exception of a tendency to blister and bubble. Cerium oxide as a mill addition, however, gave very satisfactory opacification, comparing quite favorably with tin oxide or zircon in all concentrations. Cerium enamels have high gloss but, especially in low percentages, give marked pinholing. In low concentrations, cerium is not as good an opacifier as antimony, but it is equal in opacification and gives a better white color when as much as 10% is used. Cerium frits are brown colored and clear but produce an enamel which is canary yellow as it leaves the furnace and white opaque after cooling. Frit mixtures of cerium and antimony oxides showed that high percentages of cerium with low antimony gave virtually no opacity and that a small percentage of cerium with a high antimony content increased reflectance above that of the frit containing the same concentration of opacifier when antimony alone is used. A.F.M.

Cut plant operation costs by stopping little enamel leaks. ANON. *Ceram. Ind.*, **35** [3] 54, 56, 58 (1940).—The many small economies which can be made in enamel plants to obtain substantial savings in enamel ordinarily wasted are discussed. Illustrated. A.F.M.

Determining the mechanical strength of enameled ware. N. S. KHARCHENKOVA. *Zavodskaya Lab.*, **9**, 243–44 (1940).—A device based on the fall of a steel ball held in position by an electric magnet is described. P.B. & E.S.

Effects of soluble salts present in enamel mill liquors. T. L. HURST AND A. I. ANDREWS. *Jour. Amer. Ceram. Soc.*, **24** [5] 171–78 (1941).—12 references, 9 figures.

Equipment for building an efficient enamel shop. ANON. *Ceram. Ind.*, **35** [5] 42–46 (1940).—Equipment in the Tappan Stove Co., Mansfield, Ohio, is described. Illustrated. A.F.M.

Former efforts to produce boron-poor and boron-free enamels. ANON. *Keram. Rundschau*, **48** [3] 20–22 (1940).—Literature on efforts made to obtain boron-poor or boron-free enamels is reviewed, and numerous more or less successful recipes are given. The general methods of eliminating boron are (1) the use of glass powder, by which the silicic acid is introduced in an easily melting form, (2) introduction of water glass for the same reason, (3) use of soda in larger quantities as flux, (4) use of fluorides as fluxes, making use of the reaction of fluorspar with soda, and (5) division of a batch into two melts to obtain a lower melting point. A substitute having the same specific properties as the boron-containing compounds used in the enamel industry is not available (at least in Germany), and the above-mentioned methods are successful only in special cases. M.H.

Speed drying of porcelain enamel with infrared heating lamps. ANON. *Ceram. Ind.*, **36** [3] 62, 64 (1941); see "Infrared . . . ," *Ceram. Abs.*, **20** [4] 85 (1941). A.F.M.

PATENTS

Enamel compositions containing lake pigments. E. I. DU PONT DE NEMOURS & CO. Brit. 533,639, March 5, 1941 (Aug. 16, 1938).

Opacifiers for porcelain enamels and porcelain enamels containing them. FERRO ENAMEL CORP. Brit. 534,559, March 19, 1941 (March 13, 1939).

Producing enamel, more particularly white clouded enamel. IGNAZ KREIDL. U. S. 2,236,852, April 1, 1941 (Aug. 3, 1937).—An enamel slip of controlled stiffness having incorporated therewith at least one substance capable of reducing the stiffness of the slip and selected from the group consisting of polybasic acids and acid reacting salts thereof, in a quantity ranging from 1 to 5 parts per thousand of the slip.

Glass

Additive factors for calculating the coefficient of thermal expansion of glass from its composition. KUAN-HAN SUN AND A. SILVERMAN. *Glass Ind.*, **22** [3] 114–15, 125 (1941).—Factors for thermal expansion recently published by Badger and White ("Comparison . . . ," *Ceram. Abs.*, **18** [4] 96 (1939)) are compared in tabular form with those proposed by fourteen other investigators. A.P.

Air filters from glass wool. E. V. REKK. *Otoplenie & Ventilyatsiya*, **1939**, No. 8, pp. 23–26; *Khim. Referat. Zhur.*, **1939**, No. 12, p. 118; *Chem. Abs.*, **35**, 662–63 (1941).—The materials and the technique of production of standard section of filters from glass wool saturated with an oil emulsion and their technical characteristics are described.

Anomalous depolarization of light scattering in optical glasses. R. S. KRISHNAN. *Proc. Indian Acad. Sci.*, **8A** [5] 442–47 (1938).—K. presents quantitative results based on photographic photometry, demonstrating the existence of the Krishnan effect in optical glasses. See "Scattering . . .," *Ceram. Abs.*, **16** [7] 203 (1937); "Theory . . . ," *ibid.*, **19** [6] 149 (1940). A.P.S.

Batch blanket feed ups output 10% and improves window-glass quality. ANON. *Ceram. Ind.*, **36** [2] 48–49 (1941).—At the Mt. Vernon, Ohio, plant of the Pittsburgh Plate Glass Co., the glass batch is fed to the tank in a continuously flowing blanket 20 ft. wide and 3 in. deep. This allows practically all of the material to float on the surface of the melt where it is exposed directly to the flame and is soon put in solution. The method also reduces dust and almost entirely eliminates seeds. The tank is equipped with a suspended charging end wall which may be raised or lowered to control the thickness of the batch blanket. Illustrated. A.F.M.

Chemical compositions and water solubilities of glasses: VIII. S. NAGAI AND M. MASUDA. *Jour. Japan. Ceram. Assn.*, **46**, 525–30 (1938); *Chem. Abs.*, **34**, 6781 (1940).—A second series of titania glasses was prepared by replacing SiO_2 (72%) with TiO_2 in the amounts of 5, 10, 15, and 25%. The second series of titanate glasses is stronger and more stable. For Parts VI and VII see *Ceram. Abs.*, **18** [3] 70 (1939).

Colored glass marbles widely used in industry. ANON. *Ceram. Ind.*, **35** [3] 52–53 (1940).—The manufacture and uses of glass marbles are described. The annual world consumption is about 250 million. A table of 11 colored-glass batches for marbles is given. A.F.M.

Control of protective glasses for dangerous rays. C. MAURELLI. *Securitas* [Milan], **27**, 57–62 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 1067.—Standard specifications for protective glasses adopted in the U. S., England, Germany, and Switzerland and the need for similar standards in Italy are discussed. M.V.C.

Corning makes Christmas-tree ornaments. ANON. *Bull. Amer. Ceram. Soc.*, **20** [4] 148–49 (1941).—1 photograph.

Data on the melting performance and heat consumption of tank furnaces. R. GUENTHER. Translated in *Glass Ind.*, **22** [2] 66–68 (1941); see "Nomogram . . . ," *Ceram. Abs.*, **20** [3] 66 (1941). A.P.

Definition of glass. ANON. *Glass Ind.*, **22** [2] 64–65 (1941).—A dozen definitions of glass are quoted and criticized. Definitions by G. W. Morey in Properties of Glass (*Ceram. Abs.*, **18** [2] 48 (1939)), and by H. Moore ("Glasses . . . ," *ibid.*, **19** [8] 186 (1940)) are recommended. **Discussion.** F. W. PRESTON. *Glass Ind.*, **22** [3] 108 (1941). A.P.

Diffusion of helium and of hydrogen through Pyrex brand chemically resistant glass. NELSON W. TAYLOR AND WILLIAM RAST. *Jour. Chem. Phys.*, **6**, 612–19 (1938); *Chem. Abs.*, **32**, 9419 (1938).—The effect of heat-treatment on the rate of diffusion of H_2 at 512° and He at 180° to 590° through Pyrex brand glass was determined. The rate of diffusion is directly proportional to the pressure for both gases. The diffusion data throw light on the processes of molecular rearrangement involved in stabilization of the glass. Below 548° the rates of diffusion (R) were increased about 10% by giving the glass sufficient heat-treatment to assure "stabilization," i.e., equilibrium in the processes of dissociation and association. This increase occurred despite the fact that such heat-treatment normally increases the density of the glass and therefore points to a chemical theory rather than a simple theory of holes governing the diffusion process. There was a continuous linear dependence for the stabilized glass of log R on $1/T$ from 440° to 590°. This range extends into the region of a true viscous liquid, and it follows that the properties of a stabilized glass are continuous with those of a viscous liquid and that there is no need to postulate a separate glassy state. The "transformation point" mentioned by some investigators is merely the temperature of rapid strain release of an unannealed sample. At or near 440° the log R vs. $1/T$ curve takes a lesser slope for lower temperatures, and this change is attributed to the loss of rotational or vibrational freedom in the silicate complex, analogous to that frequently found in dielectric studies on solids. Activation energies are calculated for the two temperature ranges. At 512° the rate of He diffusion is 45 times that of H_2 because of chemical forces which delay the progress of H_2 through the silicate network. Gas diffusion furnishes a highly sensitive method for studying the molecular condition of silicate glasses and similar materials.

Effect of heat and moisture on the strength and tension of glass silk and fiber. PAUL AUGUST KOCH AND GÜNTHER SATLOW. *Klepzigo Text.-Z.*, **43**, 542–47 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 1196.—The effect of temperatures up to 500° on the strength and tension of glass silk and fiber was tested for different periods of time. After a certain temperature (250° for glass silk and 320° for glass fiber), no decrease in strength occurs with longer heating. Below these temperature limits, the strength decreases considerably, even when the fiber is heated for less than 1 hr., and it does not increase noticeably with longer heating time. The breaking length of the fiber must be calculated for each series of experiments on the basis of different determinations, and every separate value for the fineness of the fibers must be determined. The tension, which is very low to begin with, decreases with higher temperatures and longer heating time. See "Technological . . . ," *Ceram. Abs.*, **20** [1] 14 (1941). M.V.C.

Effect of lithium in glass. O. PŘIDAL AND Z. SCHAEFER. *Skláfské rozhledy*, **17** [2] 25–28 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 1196.—Experiments on the effect of replacing soda by Li_2CO_3 in the smelting of Na_2O-CaO silicate glasses and the addition of lepidolite showed that the use of Li_2O as a constituent of the glass batch has many advantages. The Li_2O glasses smelt and fine well. Li_2O in small amounts can be used in place of Na_2O for the purpose of smelting glasses with a low expansion coefficient. The softening point is low. Li_2O glasses with Al_2O_3 fuse well and have good resistance to chemicals. The Li_2O and the lepidolite found in Moravia may contain only 0.15% Fe_2O_3. M.V.C.

Fused bifocals. G. F. DAINTY. *Optician*, **100** [2584] 131–34 (1941).—D. gives a detailed account of the history, theory, and manufacture of fused bifocal lenses. The two glasses used are of different refractive index. Scrupulous cleanliness of surfaces is essential for the fusing operation, which is carried out in electric heaters at fusion temperatures; a slow annealing process follows. M.B.H.

Glass-bottle industry. Comments upon technical matters from within. C. J. PEDDLE. *Jour. Soc. Glass Tech.*, **22**, 332–56 (1938); *Chem. Abs.*, **33**, 7976 (1939).—The problems of suitable raw materials, proper furnace efficiency, and satisfactory refractories are generally discussed. The increase in Fe_2O_3 in sand during transportation and in storage is given special treatment, the increase being as much as from 0.026% to 0.041% from source to destination after storage for 9 months.

Glasses which absorb infrared. HANS FREYTAG. *Umschau*, **45** [3] 35–37 (1941).—Sixty per cent of the radiation of the sun and 80% of that of electric bulbs are infrared. SiO_2 in glass absorbs much of the radiation between 28,000 and 35,000 a.u. and all radiation over 50,000. Boric and phosphoric acids absorb radiation over 20,000 a.u., and glass with 2% FeO absorbs 99% of all infrared above 10,000 a.u. Other metal oxides are also good in certain ranges. Glasses which are 50% transparent for green are transparent for infrared between 8000 and 20,000 a.u.; FeO glasses are 5 to 18% transparent, copper glass 47%, nickel glass 86%, and cobalt glass 88%. Characteristics for different brands are given but not their compositions. J.M.N.

Hartford-Empire Co. develops new system of glass-melting. ANON. *Glass Ind.*, **22** [2] 53–56, 80 (1941).—Two measuring feeders, delivering through a covered triangular doghouse, automatically distribute islands of batch through the tank according to a pattern worked out individually for each furnace. The batch is fritted in the doghouse, eliminating carryover. The automatic operating system includes a glass-level gauge and a control panel. Illustrated. A.P.

How the old timers made glass. C. H. MODES. *Ceram. Ind.*, **35** [3] 62, 64 (1940).—M. reviews recipes for green and clear bottle glasses compounded in the 16th to 18th centuries. A.F.M.

Improve bottle quality, lower cost through lightweight design. ANON. *Ceram. Ind.*, **35** [5] 37–39 (1940).—Factors of design and plant-operating practice underlying the trend toward lightweight glass containers are discussed. The unit cost of fuel, batch materials, furnace refractories, and transportation is reduced. Increased mechanical breakage of thinner container walls is more than offset by decreased losses due to thermal breakage. Stippling increases the thermal shock factor. Machine operating speeds on lightweight containers are usually only slightly faster but sometimes increase as much as 20%. Illustrated. A.F.M.

Improving durability of glass surfaces by treatment with volatile salts. A. E. BADGER AND R. R. ROUGH. *Glass Ind.*, **22** [3] 109–10 (1941).—Specimens of sodium borosilicate glass of poor durability were exposed for 1 hr. at controlled temperatures between 350° and 500°C. to the action of metal chlorides. The durability of the specimens was compared with that of the untreated glass by immersion in 10% citric acid solution for 10 min. The durability was improved by the chlorides of vanadium, aluminum, cobalt, nickel, manganese, and silicon, but no favorable results were noted with the use of bismuth, zinc, tin, and iron chlorides. A.P.

Inspection methods at Diamond Glass Co. ANON. *Glass Ind.*, **22** [3] 101–103 (1941).—A six-year program of modernization has brought this factory the latest in glass-house equipment. The ratio of rejected ware remains higher than that for most plants because of the rigid system of inspection. 11 photographs. A.P.

Insulating materials—elimination of fire risks—application of glass fibers. A. R. DUNTON. *Electrician*, **126** [3270] 58 (1941).—The best methods of eliminating fire hazards in connection with electrical apparatus have been studied. There has been a tendency to increase the permissible temperatures generally associated with electrical motors and generators, with the result that the materials employed must be most carefully selected. Improvements have been achieved by the use of woven glass insulating tape, fabrics, and sleevings which are now being produced in England combined with high-temperature insulating varnishes of the Glyptal type. These glass insulating materials can be obtained in very thin varieties and are therefore being extensively used for the insulation of magnet wires. In many cases long-length glass fibers are being employed in place of cotton where the latter material has

been used for the reinforcement of asbestos tapes, ribbons, and coverings for wires. It is claimed that, by the use of a first layer of glass followed by a second layer of asbestos, an improved type of heat-resisting conductor can be obtained which combines the excellent electrical properties associated with glass with the tough cushioning effect of the asbestos. H.K.R.

Laminating Hi-Test safety glass at Libbey-Owens-Ford Glass Co. ANON. *Glass Ind.*, **22** [3] 116–17 (1941).—Processes in the production of vinyl resin glass sandwiches are described. A.P.

Melting of flint glass in tank furnaces. SHURENKOV. *Keram. & Steklo*, **14** [1] 29 (1938); *Jour. Soc. Glass Tech.*, **23** [95] 18A (1939).—As a result of tests carried out with the Korolev method (*Keram. & Steklo*, **1934**, No. 11) during 1936 and 1937, it is shown that tubing and rod can be produced in tanks without risking inhomogeneity and reduction to Pb. A lowering of the tank temperature from 1380° to 1170° and that of the heating chamber from 1360° to 1090° and a decrease in losses due to breakage were obtained. The composition of the glass used was SiO_2 69.3%, Na_2O 11.0, K_2O 5.7, CaO 3.9, and PbO 10.1. The furnace, continuously in use for 14 months and 20 days, had a daily output of 700 kgm. per m.². Air and waterjacket cooling were used.

Method of obtaining mineral wool. Z. I. PERKAL AND A. S. EPSHTEĬN. *Prom. Stroitel. Materialov*, **2** [8] 79–82 (1940).—A laboratory apparatus with a rapidly rotating element produces wool by centrifugal force. The method is more efficient than other methods used and gives wool free from globules. P.B. & E.S.

Modulus of elasticity and damping in relation to the state of the material. F. FORSTER AND W. KOSTER. Inst. Elec. Engrs. Discussion on Nondestructive Testing, pp. 41–47 (Nov. 25, 1938); *Jour. Soc. Glass Tech.*, **23** [98] 249A (1939).—Test bars 200 mm. in length and 10 mm. in diameter were supported on two wires. One end of each wire was fixed to a leaf spring, the other ends being attached to an electrically oscillated buzzer and an amplifier. It was thus possible to determine the natural frequency of the test piece and calculate its modulus of elasticity. The effect of temperature, annealing, grain size, etc., on the elasticity and damping of a number of metals and alloys was determined.

Necessity of microscopic analysis in evaluating the quality of glass sand. A. M. TSEKHOMSKIĬ. *Zavodskaya Lab.*, **9**, 251–53 (1940).—T. emphasizes the necessity of mineralogical and chemical analyses for the evaluation of glass sands. See "Microscopic . . . ," this issue, p. 152; "Concentration . . .," *Ceram. Abs.*, **19** [6] 147 (1940). P.B. & E.S.

New uses for glass. S. R. SCHOLES. *Glass Ind.*, **21** [4] 185, 201 (1940).—Glass has two important properties, transparency and chemical durability, and whatever has been done in recent years to extend the usefulness of glass has depended largely on the increasing ability of technologists to vary and control these properties. The workability of glass, in its transition from fluidity to rigidity, has caught the imagination of many inventors and designers. A.P.

Oxygen ion in oxide glasses. TOSIO ABE. *Proc. Phys.-Math. Soc. Japan*, **22**, 647–65 (1940); *Chem. Abs.*, **35**, 863 (1941).—The molecular refractions of the glasses in the ternary systems SiO_2–Na_2O–CaO, SiO_2–K_2O–CaO, and B_2O_3–Na_2O–SiO_2 were studied, and the most probable values of molecular refraction were calculated on assumptions from experimental and theoretical deductions that along the lines of constant Na_2O content the molecular refraction varies linearly with the molecular concentration of the oxide in the glass. The ionic refraction for such an oxygen ion was calculated as a function of the molecular concentration of Na_2O, and it appears that the ion refraction-concentration curve shows the stability (the relative difficulties of crystallization) of glasses. In the case of B_2O_3–Na_2O–SiO_2 it is shown that for a Na_2O content greater or smaller than 0.18 the ionic refraction of an O ion belonging simultaneously to a BO_3 triangle and a BO_4 tetrahedron is less or larger than that of an O ion belonging to two BO_3 triangles at the same time. It is also shown that the addition of Na_2O to a SiO_2 glass results in a continuous increase in the specific volume, while in the case of a B_2O_3 glass it first decreases to a minimum and then gradually increases until, at 0.19 mol. % Na_2O, it increases as in the case of SiO_2–Na_2O glasses. A. concludes that B atoms change from triangular to tetrahedral coordination until one fourth of the BO_3 triangles change to BO_4 tetrahedra and are unaffected by further additions of Na_2O. This change of coordination of B atoms is thought to be the cause of the abnormal properties found in these glasses. 20 references.

Proper use of the stress tester. M. FANDERLIK. *Sklářské rozhledy*, **17** [2] 32–35 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 1067.—F. gives instructions for using the polarization apparatus in the glass industry for controlling annealing by determining the direction and type of stresses. M.V.C.

Rapid etching method and etching specifications. OTTO HERFURTH. *Diamant*, **62** [35–36] 235–36 (1940).—A rapid immersion etching method developed by Arnot (*Ceram. Abs.*, **15** [8] 234 (1936)) which produces particularly good mat white tones is described. The bath is composed of 2 parts by weight of HF (60 to 65%), 4 parts ammonium fluoride, and 1 part crystallized soda. The solution is made in a Pb or gutta-percha container. When the ammonium fluoride is completely dissolved, the soda is added little by little. The glass is cleaned before etching in a 3% HCl solution and then immersed for about 3 min. and moved around in the bath. It is rinsed well in water, cleaned with brushes in warm water, and rinsed again in warm water. By changing the amount of soda in the bath, the tones of the white etching can be varied within wide limits. The temperature of the bath should not be below 40°C. The glass can be polished by immersion for 15 to 30 sec. in 75 to 80% HF with $9H_2SO_4$ in $8H_2O$; lead glasses require stronger polishing acids than soda-lime glasses. M.H.

Selection of combustion equipment for uniform day-tank operation. HOWARD R. PARMAN. *Ceram. Ind.*, **35** [3] 36–38 (1940).—New burner equipment gives glass of constant viscosity, reduces the use of coloring agents from 18% to 10%, makes the melting time directly proportional to the fills, promotes uniformity of melting, eliminates stones and devitrified scums, lengthens the life of the refractories, minimizes burner adjustments, and reduces fuel consumption. The specifications for the equipment state that the burner must produce a full luminous flame, develop a temperature of over 2600°F., work with the same efficiency on the batch charge as on the melt during plaining, avoid throwing heat on the operators, and possess simple and constant adjustment, close flame control, automatic gas-air ratio control, and a single volume control. Illustrated. A.F.M.

Soldered metal-to-glass or porcelain seals. S. T. MARTIN. *Rev. Sci. Instruments*, **11** [6] 205–206 (1940).—Copper and brass tubing has been successfully soldered to Pyrex brand tubing by turning the wall thickness of the tubing down to about 10 or 20 mils for a distance of about $^1/_8$ in. from the end and spinning the end of this out to form a small flange on which the end of the glass tubing rests. The glass tubing is first metallized with silver by means of silver oxide or Burnishing Silver Paste (Hanovia Chemical Co., Newark, N. J.). A flux of tartaric acid (concentrated solution in water), to which has been added $^1/_4$ to $^1/_3$ its volume of glycerine, is used with a solder of 70 tin and 30 lead or 60 tin and 40 lead to complete the seal. H.E.S.

Structure and optical properties of iridescent glass. C. V. RAMAN AND V. S. RAJAGOPALAN. *Proc. Indian Acad. Sci.*, **9A** [5] 371–81 (1939).—A study of numerous specimens and of 30 photomicrographs of them shows that the structures in decomposed glass may be divided into six categories exhibiting distinct optical phenomena. The colors of decomposed glass actually become more striking when the material is covered by liquid. A.P.S.

Sulfates in glass. A. B. SCHOLES. *Glass Ind.*, **22** [3] 111–13, 126–28 (1941).—S. reviews the literature per-

taining to the history of the use of sulfates in glass, their chemical and physical actions, and their effects on melting, fining, refractory attack, decolorizing, and the glass surface. 62 references. A.P.

Tantalum glass: K_2O–Ta_2O_5–SiO_2 series. KUAN-HAN SUN AND ALEXANDER SILVERMAN. *Jour. Amer. Ceram. Soc.*, **24** [5] 160–67 (1941).—25 referenees, 5 figures.

Three acres of safety glass a day made in new Ford plant. ANON. *Ceram. Ind.*, **36** [3] 43–45 (1941).—The equipment and processes used in the manufacture of laminated safety glass at the plant of the Ford Motor Co., Detroit, Mich., are described. Vinyl plastic is received in large rolls; it is passed through a set of brushes to remove the excess soda with which it is coated to prevent sticking in shipping and handling, then through drying ovens to remove intercellular moisture, and over a set of cooling rolls into the cutting room. Sheets are cut to the size and shape of the glass and stored until needed. The cut sheets of vinyl are passed through a continuous spray washer and then through another drier. After inspection under polarized light, they are carried to the laminating room where the glass is introduced from a set of washers. Each piece of plastic is put between two sheets of glass which are carried on to prepress operations and final pressing in an autoclave. Accurate and specific temperatures and humidity conditions are maintained in each department with elaborate air-conditioning apparatus. Illustrated. A.F.M.

Twenty years of progress in annealing. C. CONE. *Glass Ind.*, **21** [4] 182–84 (1940).—Annealing lehrs in use today are almost entirely a development of the present generation. Improvements have taken place in the conveyer, the enclosure, the heating equipment, and in automatic temperature control. Developments in decorating lehrs are receiving increasing attention. A.P.

Twenty years of progress in glassware molds. ANON. *Glass Ind.*, **21** [4] 180–81 (1940).—Improvement in the operating characteristics of glass molds has resulted from continuous trial of different materials, together with advances in the technique of mold manufacture in both foundry and machine shop. Most molds are still made of gray iron cast against a chill. Some requirements can be met only by the utilization of alloys of iron with chromium, nickel, vanadium, molybdenum, copper, and aluminum. Advances in the foundry and machine shop and in design and maintenance are sketched. A.P.

Ultramodern production methods used in glass-block manufacture. ANON. *Ceram. Ind.*, **35** [6] 40–44 (1940).—The manufacture of hollow glass block at the Port Allegheny, Pa., plant of the Pittsburgh Corning Corp. is described. About 30% of cullet is used with the batch charge. The combustion air is held constantly at 130°C. The block are made by forming two halves resembling shallow square dishes and then sealing these into a hollow vapor-tight unit. The seal is made by reheating the four edges of each half block to 1100°C., blowing out the products of combustion, and pressing the two halves together with 50 lb. pressure (for an 8-in. block). Quantitative measurements of residual annealing strain are taken hourly. Illustrated. A.F.M.

Up output 12% on bottle melting unit with luminous flame control. ANON. *Ceram. Ind.*, **36** [3] 56–58 (1941).—Luminous flame control on a 4-port regenerative furnace at the Hart Glass Div., Armstrong Cork Co., Dunkirk, Ind., allows a daily production of 112 tons compared with 100 tons formerly produced. The most important feature of the combustion-control system is the use of a part of the combustion air with the gas and the dilution of this air by waste gases which are recirculated back to the tank from the duct leading to the exhaust stack. As these exhaust gases are practically inert, their use with the fuel causes the flame to lengthen. By varying the amount of waste gases used with the incoming fuel, the flame can be made to reach just across the furnace under all conditions. This extremely accurate control of flame length allows the development of a blanket of flame with maximum coverage which may be adjusted to prevent burning of fuel in the outgoing checker chambers. The novel batching setup is also described. In order to keep an accurate record of the amount of glass melted, the batch and cullet are weighed out at the doghouse as they pass from storage hoppers into charging hoppers. A heating-up furnace for spare feeder parts is built immediately adjacent to the end of one of the ports; it thereby gains a large part of the required heat from the tank furnace. Illustrated. A.F.M.

Viscosity and structure of fused quartz glass. N. V. SOLOMIN. *Zhur. Fiz. Khim.*, **14**, 235–43 (1940).—S. constructed an apparatus of the type of the Grebenschikov viscosimeter to measure the viscosities of fused substances at temperatures up to 2000° to 2200°C. In the range 1720° to 2000°, the viscosity of pure quartz glass varies between the limits of 2.83×10^4 (at 2000°) and 2.94×10^6 poises (at 1720°). In the viscosity interval $\eta = 10^4$ to 10^{12}, the viscosity-temperature relation is expressed within ±10° by the equation $\log \eta = \frac{2074}{t - 182} - 6.991$. Fused quartz glass seemingly consists of aggregates including n Si atoms and $2n$ O atoms; in the 1300° to 2000° interval, n is equal to a few hundreds and is in an inversely linear relation to the temperature. In regard to its internal structure, the agregate seemingly forms a combination of Si-O tetrahedra, conforming to the Zachariasen-Warren conceptions. P.B. & E.S.

War decoration of window fronts. *Anon. Glaces & Verres*, July–Nov., 1939; abstracted in *Glass Ind.*, **21** [2] 67 (1940). A.P.

World trade in glass, 1920–1938. E. J. DETGEN. *Glass Ind.*, **21** [4] 186–89, 198, 200 (1940).—The world's annual production approximates $800,000,000. Trends are shown graphically and discussed for the period 1920–1938 for glass in general and in the specific fields. A.P.

SEPARATE PUBLICATION

Glass Manufacture. *Carnegie Inst. Tech. Bull.*, No. 85, 187 pp. (1940).—A bibliography of articles published during 1939 covering all subjects associated with the manufacture of glass is presented. B.C.R.

PATENTS

Apparatus for the manufacture of bent tempered sheets of glass. GERALD WHITE (Libbey-Owens-Ford Glass Co.). U. S. 2,235,969, March 25, 1941 (Dec. 28, 1937).

Apparatus and method for homogenizing molten glass in forehearths, etc. D. W. MUELLER (Hartford-Empire Co.). U. S. 2,238,800, April 15, 1941 (Jan. 26, 1939).

Apparatus and method for nodulating fibers. F. E. ALLEN AND H. V. SMITH (Owens-Corning Fiberglas Corp.). U. S. 2,219,285, Oct. 29, 1940 (March 7, 1936).

Apparatus for sealing metal to glass. BRITISH THOMSON-HOUSTON CO., LTD. Brit. 534,586, March 26, 1941 (March 16, 1939).

Building block and facing tile. RUDOLPH KALKUSCH (Libbey-Owens-Ford Glass Co.). U. S. 21,771, April 15, 1941 (Oct. 19, 1938); reissue of original 2,058,235, Oct. 20, 1936 (March 13, 1936).

Coated glass articles and method of manufacturing. BERNARD LONG (Soc. Anon. des Manufactures des Glaces & Produits Chimiques de St. Gobain, Chauny & Cirey). U. S. 2,236,911, April 1, 1941 (July 2, 1934).—The method of coating a glass article with a metallic substance comprises the step of depositing the metallic substance upon at least a part of a surface of the glass article while the glass article is in a tempered state and while the temperature of the glass article ranges between 400° and 200°C.

Coating bodies with glass or other fusible mineral substance. BRITISH THOMSON-HOUSTON CO., LTD. (Tokyo Electric Co., Ltd.). Brit. 533,835, March 5, 1941 (Dec. 4, 1939).

Compound glass sheet. J. H. LEWIS (Blue Ridge Glass Corp.). Can. 395,450, March 25, 1941 (Sept. 28, 1939; in U. S. Nov. 25, 1938). G.M.H.

Device for electrically heating drawing kilns for sheet glass. E. V. BOREL (Soc. Anon. des Manufactures des Glaces & Produits Chimiques de St. Gobain, Chauny & Cirey). U. S. 2,236,231, March 25, 1941 (Nov. 5, 1937).

Drive mechanism for glassforming machines. G. M. S. Corp. Brit. 534,625, March 26, 1941 (Sept. 3, 1938).

Enamels, particularly those applicable to electric lamp bulbs. British Thomson-Houston Co., Ltd. Brit. 534,556, March 19, 1941 (March 11, 1939).

Glass distilling head. E. F. Kelm (Corning Glass Works). U. S. 2,238,174, April 15, 1941 (Jan. 3, 1939).

Glass for electric lamp bulbs. Jérôme & Bonnefoy & Cie S. à R. L. Fr. 845,726, Aug. 31, 1939; *Chem. Abs.*, **35**, 1198–99 (1941).—A glass that absorbs violet, blue, and green and allows all the other rays to pass through with a high transmission coefficient is made from sand 100, NaOH 40, $CaCO_3$ 17, CdS 4.5, and SeS 1.2 parts.

Glass fibers. Chance Bros. & Co., Ltd. (N. V. Mij. tot Beheer en Exploitatie van Octrooien). Brit. 512,875, Oct. 11, 1939 (March 25, 1938).

Glass mirrors. D. B. Nacmias and Joris Glass Industries, Ltd. Brit. 533,986, March 12, 1941 (Dec. 1, 1939).

Glass-tempering apparatus. G. W. T. Bird (Pilkington Bros., Ltd.). Can. 395,337, March 18, 1941 (March 5, 1940). G.M.H.

Glassware lehr and annealing method. F. E. Dorsey (Hartford-Empire Co.). U. S. 2,238,791, April 15, 1941 (June 3, 1938).

Increasing the sound-absorptive properties of cellular glass. E. H. Haux (Pittsburgh Plate Glass Co.). U. S. 2,237,032, April 1, 1941 (Feb. 19, 1938).

Insulator press. W. C. Weber (Corning Glass Works). U. S. 2,238,198, April 15, 1941 (March 19, 1938).

Laminated safety glass. G. B. Watkins (Libbey-Owens-Ford Glass Co.). U. S. 2,236,046, March 25, 1941 (Oct. 16, 1933).

Making glass. British Thomson-Houston Co., Ltd. (J. Ferguson). Brit. 533,954, March 12, 1941 (July 21, 1939).

Making glass enclosures. British Thomson-Houston Co., Ltd. Brit. 534,178, March 12, 1941 (Jan. 12, 1939).

Making hollow glass building blocks. H. H. Blau (Corning Glass Works). U. S. 2,238,153, April 15, 1941 (March 3, 1938).

Manufacture of glass. British Thomson-Houston Co., Ltd. (J. Ferguson). Brit. 533,956, March 12, 1941 (July 22, 1939).

Manufacture of multicellular glass. Soc. Anon. des Manufactures des Glaces & Produits Chimiques de St. Gobain, Chauny & Cirey. Brit. 533,763, March 5, 1941 (Dec. 20, 1938).

Method and apparatus for producing fibrous material. J. H. Thomas and G. M. Lannan (Owens-Corning Fiberglas Corp.). U. S. 2,219,346, Oct. 29, 1940 (Aug. 19, 1936; renewed Jan. 12, 1940).

Method and apparatus for the production of fine filaments of glass. W. J. Woods (Owens-Corning Fiberglas Corp.). U. S. 2,238,204, April 15, 1941 (April 22, 1937).

Method and batch for making colored glass. H. A. Truby (Pittsburgh Plate Glass Co.). U. S. 2,237,042, April 1, 1941 (April 23, 1938).—A coloring composition for imparting a permanent red color to glass comprises a mixture of small amounts of a gold halide and selenium.

Polished glass strip producing apparatus. G. H. Baillie and F. B. Waldron (Pilkington Bros., Ltd.). Can. 395,171, March 11, 1941 (Feb. 17, 1939). G.M.H.

Preparing cellular glass. W. O. Lytle (Pittsburgh Plate Glass Co.). U. S. 2,237,037, April 1, 1941 (Nov. 8, 1937).

Pressing laminated glass. J. H. Boicey (Libbey-Owens-Ford Glass Co.). U. S. 2,235,958, March 25, 1941 (Feb. 26, 1937).

Tank for molten glass. Joseph Gaskell (Pilkington Bros., Ltd.). Can. 395,336, March 18, 1941 (Sept. 11, 1939). G.M.H.

Tempering glass. Edoardo Ferlito. U. S. 2,237,982, April 8, 1941 (Dec. 16, 1937).

Tempering glass plates and sheets. Bernhard Engels. U. S. 2,237,343, April 8, 1941 (Jan. 22, 1938).

Structural Clay Products

Brick for the construction of cavity walls. R. S. *Rev. Matériaux Construction Trav. Publics*, No. 360, pp. 98–99B (1939).—In the building of cavity walls, popular in England, there is a great deal of waste in mortar which projects beyond the brick into the interior cavity and in mortar drippings. To prevent this waste, R. E. Haskwell, Rhos-on-Sea, Colwyn Bay, has devised a brick for cavity walls, along one side of which runs a narrow flange raised the width of the layer of mortar, which acts as a stop and prevents the mortar from pushing through. The flange of some of the brick is notched to accommodate the connecting Z bars. Walls made of these brick are stronger than the usual cavity walls. See "Brick cavity . . .," *Ceram. Abs.*, **20** [3] 69 (1941). M.V.C.

Cause, action, and prevention of efflorescence. W. Kaufmann. *Ziegelwelt*, **71**, 165–67 (1940); abstracted in *Chem. Zentr.*, **1940. II**, 1197.—Efflorescence may be caused by (1) salts in the raw materials, water, or fluxes; (2) salts formed during the process of drying with flue gas; (3) salts formed during the weathering of clays containing iron pyrites; (4) salts formed because of improper firing conditions; (5) salts absorbed from the floor of the place of storage or construction; or (6) salts taken up from mortar or masonry. Sulfate salts can be rendered harmless by the addition of 1.3 times the theoretically required $BaCO_3$ content. For low-grade products with a high sulfate content, firing in a reducing atmosphere at sufficiently high temperatures is preferred. M.V.C.

Colored brick. Anon. *Chem. Trade Jour.*, p. 282 (April 8, 1938); abstracted in *Chem. Industries*, **42** [5] 546 (1938).—Brick are sprayed with the coloring agent, which may be any suitable oxide mixed with water or tar, and then dusted with a protective layer of combustible material, such as sawdust. This layer assists in drying the coloring agent and prevents the brick from sticking during firing. P.G.H.

Rationalization of the heavy ceramic industry, with special reference to the brick industry. Hans Lehmann. *Ber. Deut. Keram. Ges.*, **21** [7–8] 284–93 (1940).—In some respects, the making of brick has not changed in thousands of years. As Möser says, brickmaking is 99% hard and rough practice and only 1% theory. For the national economy it is especially necessary to prevent seasonal work. Suitability for the dry-press process may be used as a basis for the classification of clays. It must not be assumed, however, that the dry-press process is the only correct one. Everything must be considered to avoid seasonal work. The tunnel kiln is the kiln of the future. A Hoffman kiln (wet process) and tunnel kilns for wet- and dry-press methods are illustrated. Everything must be done to save manpower. W.H.H.

PATENTS

Hollow structural block. J. J. O'Leary. Can. 395,563, April 1, 1941 (April 26, 1940). G.M.H.

Masonry wall. W. C. Fuller. Can. 395,550, April 1, 1941 (May 1, 1940). G.M.H.

Means for the manufacture of brick. Yorkshire Brick Co., Ltd., and A. G. Phillipps. Brit. 533,856, March 5, 1941 (Nov. 6, 1939).

Vitreous clay conduit rest section. A. P. McDonald. U. S. 2,236,801, April 1, 1941 (March 13, 1939).

Vitreous clay conduit section. A. P. McDonald. U. S. 2,236,802, April 1, 1941 (March 13, 1939).

Refractories

Blast-furnace brick of new design. ANON. *Blast Furnace & Steel Plant*, **29** [2] 187–88 (1941).—Agnew-design brick are formed so that a section perpendicular to the long axis is a parallelogram. The brick are also tapered on the long dimension and placed with the smaller end toward the inside of the lining. Advantages cited are (1) less falling out of broken ends, (2) stronger construction, (3) broken joint construction throughout, (4) fewer horizontal joints, (5) double the number of sloping radial joints, (6) no truly vertical joints at the inner surface, and (7) more closely fitting joints. B.L.

Ceramic materials of pure oxides. E. RYSCHKEWITSCH. *Chem. & Ind.*, **57** [42] 965 (1938); *Chem. Abs.*, **33**, 8942 (1939).—Very satisfactory refractory oxides recently developed are the following sintered materials: recrystallized α-corundum, spinel, beryllia, zirconia, magnesia, and thoria. The physical, chemical, and electrical properties of these materials are given. See *Ceram. Abs.*, **19** [1] 34 (1940).

Chamotte brick in steam-boiler furnaces. R. RASCH. *Arch. Wärmewirt.*, **19**, 97–100 (1938); *Brit. Chem. & Phys. Abs.-B*, **57** [8] 909 (1938).—The properties desirable in refractory brick and factors influencing their desirability in service are discussed. Photographs showing typical failures in brick are given. See "Use. . .," *Ceram. Abs.*, **18** [8] 215 (1939).

Change in the method of firing and in the repair of open-hearth furnaces. S. SAPIRO. *Stal*, **1939**, No. 4–5, pp. 8–11. B.E.K.

Chrome-magnesite brick for lining rotary cement kilns. A. S. SOKOLOV. *Tsement*, **6** [4–5] 51–55 (1939).—The general properties of chrome-magnesite brick are described, and directions for its correct use to ensure longer life are given. P.B. & E.S.

Dehydrated dolomite brick as substitute for magnesite. A. ZHAK, B. IVANOV, AND P. KIRILLOV. *Stal*, **1940**, No. 7, pp. 38–43.—The service and life of dehydrated dolomite brick in the walls of an electric arc steel-melting furnace were studied. The authors reached the following conclusions: (1) The comparatively high CaO content of this brick does not have a destructive influence on the life of the brick in the walls of the furnace. (2) The mortar for the laying of dolomite brick is characterized by the presence of a small quantity of natural minerals, such as quartz and feldspar. The addition of slightly melting feldspar aids the binding of the mortar with brick without decreasing the refractoriness. (3) The durability of dolomite brick in the walls of an electric arc furnace is about 2 to 3 times greater than that of magnesite brick. B.E.K.

Determination of the resistance of ceramic products to sudden temperature changes. W. STEGER. *Chem. Fabrik*, **11**, 508–12 (1938); *Brit. Chem. & Phys. Abs.-B*, **58** [ ] 381 (1939).—The official German methods for testing the resistance of refractories and ceramic products to temperature changes (DIN 1068), in which the sample is heated to 950° and quenched in H_2O, are discussed, and a new process is described in which samples are subjected to sudden heating by immersion in a bath of molten metal (Sn 70, Pb 30%; melting point 185°). Three series of tests are carried out, the bath being heated to (1) 300°, 400°, 500°, etc.; (2) 250°, 350°, etc.; and (3) 275°, 325°, etc. The lowest temperature at which cracks first appear is a measure of the resistance of the sample. Ceramics may be grouped according to this temperature: (1) 250° (enamel or limestone ware); (2) 300° (feldspar ware, steatite); (3) 400° (Seger porcelain, low-resistance stoneware); (4) 600° (sintered corundum, average stoneware); and (5) 750° (hard porcelain, special heat-resistant stoneware, porous masses with more than 40% of SiC).

Determination of the spalling resistance of lightweight refractories. A. A. PIROGOV AND A. I. ROÏZEN. *Zavodskaya Lab.*, **9**, 879–83 (1940).—The standard method of testing is not satisfactory for frothed grog refractories even with air cooling; the latter can be used for refractories made by the method of burning out additions (volume weight > 1). Comparative characteristics of frothed grog refractories (volume weight < 1) can be tested by abrupt changes of temperature on small cylinders and bars cut out of the brick. Methods of indirect determination are not applicable owing to an inhomogeneity of structure of the brick. A good qualitative evaluation can be obtained by the panel method. P.B. & E.S.

Dolomite brick for metallurgical purposes. ALFRED B. SEARLE. *Iron & Steel Ind.*, **11**, 593–96 (1938); *Chem. Abs.*, **32**, 8721 (1938).

Effect of alkalis on refractories with particular reference to the gas and coking industries. H. T. S. SWALLOW. *Gas Jour.*, **216**, 422–44 (1936); *Chem. Abs.*, **31**, 837 (1937).

Effect upon furnace refractories of protective gases for high-carbon steels. JOHN H. LOUX. *Trans. Amer. Soc. Metals*, **28** [4] 877–91 (1940); see *Ceram. Abs.*, **20** [3] 70 (1941). B.C.R.

Electricity furnishes power for kyanite production in Virginia. C. E. ANDERSON. *Southern Power & Ind.*, **58** [10] 76–79 (1940); *Chem. Abs.*, **35**, 2290 (1941).—Rich kyanite ore is crushed, concentrated in a flotation plant, dried, and subjected to magnetic separation to remove magnetic material. The resultant kyanite may be sold to the ceramic trade as such or calcined to mullite.

Firing refractories. R. LEDUC. *Rev. Matériaux Construction Trav. Publics*, No. 360, p. 99B (1939).—Observations on the behavior of refractories at high temperature are given. In the firing of large pieces, the question of expansion is important; it depends on the firing temperature and the nature of the clay and varies with the content of free silica and fluxes. During firing, the fluxes dissolve the free silica and the silicate ($Al_2O_3 \cdot 2SiO_2$) contained in the brick, converting the latter into sillimanite, $Al_2O_3 \cdot SiO_2$; the free silica liberated is transformed first into tridymite and at 1470° into cristobalite. The coefficient of expansion is the smaller, the more cristobalite is formed. Other factors, such as the fineness of the silica particles, enter into the question of silica transformation in the firing of refractories. See "Refractory products," *Ceram. Abs.*, **19** [9] 216 (1940). M.V.C.

Flint clays of Ural and the refractories prepared from them. P. S. MAMYKIN AND S. G. TRESVYATSKI. *Uralskaya Metallurgiya*, **1940**, No. 2, pp. 22–28.—The physical, chemical, and technical properties of flint clays of Ural and refractories prepared from them are described. B.E.K.

Forsterite refractories prepared from Ural dunites. P. S. MAMYKIN AND V. V. SAPAROV. *Uralskaya Metallurgiya*, **1940**, No. 2, pp. 18–22.—The thermal properties of dunite, the physical and chemical bases of preparation of forsterite refractories from dunite, the recommended technological plans, the quality of forsterite refractories, and the experimental materials of the Department of Silicate Technology of the Ural Industrial Institute are described. B.E.K.

Kyanite products without clay bond. P. S. MAMYKIN AND S. G. ZLATKIN. *Uralskaya Metallurgiya*, **1937**, No. 4, pp. 44–46; abstracted in *Chem. Zentr.*, **1938, II**, 4705.—Attempts to produce ceramic refractory products from kyanite without a clay bond are discussed. A kyanite concentrate containing 61.8 Al_2O_3, 38.1 SiO_2, and 0.8% Fe_2O_3 was used. Its refractoriness was over cone 37 (1825°). M.V.C.

Manufacture of caustic soda and alumina from salt and bauxite. V. S. DUBEY, Y. P. VARSHNEY, AND R. S. SHARMA. *Proc. Nat. Acad. Sci. India*, **8**, 40–48 (1938); *Brit. Chem. & Phys. Abs.-B*, **57** [12] 1409 (1938).—The process has been evolved to utilize raw materials available in India. Barytes from Alwar State (SiO_2 2.82, Al_2O_3 0.28, Fe_2O_3 0.11, BaO 62.78, CaO 0.94, MgO 0.76, SO_3 32.38%) and bauxite from Katni (SiO_2 1.85, Al_2O_3 58.83, Fe_2O_3 3.50, TiO_2 6.11, CaO + MgO 0.08, volatile matter 28.80%) were ground together to less than 200-mesh and heated at 1150° to 1500° (optimum 1400°) in varying

proportions, of which the best was 100:60 with 1% of added C; 60% of the BaO could be extracted with H_2O in the form of $BaO \cdot Al_2O_3$, and the remainder of the BaO and Al_2O_3 could be recovered as sulfates, the SO_3 produced b ing used to convert the NaCl into Na_2SO_4. The solution of $BaO \cdot Al_2O_3$ by seeding with $Al(OH)_3$ and NH_4Cl yields $Al(OH)_3$, the filtrate from which with Na_2SO_4 gives $BaSO_4$ and % NaOH solution. The process is successful on a semicommercial scale.

Manufacture of multigrog saggers. R. T. MAKHL. *Keram. Sbornik*, **1940**, No. 8, pp. 14–21.—Multigrog saggers are superior to ordinary grog saggers, but this superiority depends upon the properties of the grog (waste sagger grog). M.V.C.

Magnesia refractories: I. M. MITA. *Jour. Japan. Ceram. Assn.*, **49** [577] 25–29 (1941).—M. studied the change in the chemical and physical properties of dolomite and magnesite by calcining. The change of weight was studied by a thermobalance. The dissociation of magnesite in a CO_2 atmosphere begins at 520°C. and ends at 700°C. In the case of dolomite, $MgCO_3$ dissociates between about 560° and 860°C.; the dissociation of $CaCO_3$ begins at about 860°C. and ends at 980°C. The heats of dissociation were also determined: that for magnesite was 387.31 Cal. per gm., and that for dolomite was 281.09 Cal. per gm. Dolomite and magnesite were calcined at various temperatures, and their specific gravity, crushing strength, and shrinkage values were determined.

Calcined temp. (°C.)	Magnesite		
	Sp. gr.	Strength (kgm./cm.²)	Shrinkage (%)
Room temp.	3.02	975	0
100	2.97	1052	0
200	2.97	1021	0
300	2.97	998	0
400	2.97	960	0
500	2.98	872	0
600	3.06	755	0
700	3.38	314	0
800	3.52	42	0.4
900	3.49	27	3.08
1000	3.43	15	6.67
1100	3.50	10	7.54
1200	3.56	17	9.75
1300	3.58	15	11.00
1400	3.57	15	10.54
1500	3.59	15	9.26

Calcined temp. (°C.)	Dolomite		
	Sp. gr.	Strength (kgm./cm.²)	Shrinkage (%)
Room temp.	2.87	1992	0
100	2.86	2013	0
200	2.85	1956	0
300	2.86	1930	0
400	2.85	1946	0
500	2.87	1996	0
600	2.86	2003	0
700	2.86	1878	0
800	2.89	1430	0
900	2.92	993	0.1
1000	3.02	298	0.4
1100	3.20	194	1.68
1200	3.31	189	3.09
1300	3.33	207	5.52
1400	3.35	219	6.43
1500	3.36	251	7.44

The deformation under load (kgm. per cm.²) was also studied. The specific heat of magnesite increases from 0.2231 Cal. per gm. at room temperature to 0.2690 Cal. per gm. at 650°C.; it then decreases with dissociation up to 850°C.; after dissociation is complete it again increases. Similar results were obtained for dolomite. The thermal conductivity was measured, and the results are as follows:

Temp. (°C.)	Thermal conductivity (cal./cm. sec. °C.)	
	Magnesite	Dolomite
200	0.00845	0.00600
300	0.00727	0.00560
350	0.00702	0.00542
400		0.00525
500		0.00501

X-ray studies showed periclase in the magnesite which was calcined at 800°C.; the lines of periclase became very clear and strong at 1000°C. In dolomite no change was observed up to 600°C.; at 800°C. it changed to periclase and calcite; above 1000°C. it became periclase and CaO. Y.K.

Method of increasing the refractory properties of kaolin and clays. P. P. BUDNIKOV AND A. N. SYSOEV. *Zhur. Priklad. Khim.*, **13**, 719–22 (1940).—For the purpose of obtaining a highly refractory silicon carbide corundum material, a batch consisting of kaolin and clay with an excess of coal was prepared without an addition of metallic iron. In this way the formation of ferrosilicon was obviated, and all of the reduced silica combined with surplus carbon, giving SiC according to the reaction $Al_2O_3 \cdot 2SiO_2 + 6C = Al_2O_3 + 2SiC + 4CO$. The reaction between kaolin and coal begins at 1450°C. and ends at about 1700°C. A refractory was obtained by mixing the product with 10% plastic refractory clay and calcining it. Its melting point was 1880°C. Its deformation under load approximates its melting temperature. P.B. & E.S.

Monolithic bottom for heating furnaces. S. BESEDIN. *Novosti Tekhniki*, **1939**, No. 35–36, pp. 20–21.—Alumina silicate cement prepared from blast-furnace slags was used for the monolithic bottom. It had the following composition: SiO_2 6.54, Al_2O_3 50.24, Fe_2O_3 2.68, and CaO 36.81%. B. describes the process of preparation of the cement and the bottom. A monolithic bottom was used for temperatures up to 1100°C., and it did not require repair even after 6 months. B.E.K.

Practical application of hot-face insulating brick. J. W. JACKSON. *Metallurgia*, **18**, 206–208 (1938); *Chem. Abs.*, **33**, 333 (1939).—In some furnaces, economies result from using insulating brick for the interior lining; the heat capacity of furnace walls is thus decreased. Properties of insulating brick are discussed.

Preparation of refractory material high in alumina. A. BAZILEVICH. *Novosti Tekhniki*, **1938**, No. 11–12, pp. 12–13; *Chem. Abs.*, **32**, 7689 (1938).—Kaolin or clay is calcined at 1000° and treated with boiling NaOH solution. The solid residue, of the approximate composition $3Al_2O_3 \cdot 2SiO_2$, is washed, dried, and mixed with 10% of plastic refractory clay. The mixture is briquetted, fired at 1500°, crushed, and milled. This product is mixed with 25% of clay or kaolin, briquetted, and fired at 1600°. The brick obtained contain 57% Al_2O_3. The material is thermostable at 1820°. The solution obtained in digesting clay yielded NaOH and $CaSiO_3$ on treatment with slaked lime.

Preparation of silicocalcium. VARZANOV, NEGOVSKIĬ, IZRAILOVICH, AND A. KRAMAROV. *Novosti Tekhniki*, **1938**, No. 3, p. 17; *Chem. Abs.*, **32**, 4439 (1938).—SiCa was prepared by smelting in the electric furnace silicon carbide 20, CaC_2 46, and quartz 34%. The product contained 32 to 37% Ca and less than 1.5% Fe.

Production of pure Al_2O_3 from aluminum sulfate. S. BRETSZNAJDER. *Przemysl Chem.*, **22**, 285–90 (1938); abstracted in *Chem. Zentr.*, **1939**, **II**, 4550.—$Al_2(SO_4)_3$ was purified and calcined. The decomposition of $Al_2(SO_4)_3$ depends on the velocity of formation of SO_3. The decomposition is obtained at 830° to 900°; Al_2O_3, however, becomes hygroscopic to such an extent that working temperatures of 1200° to 1300° are recommended. See *Ceram. Abs.*, **19** [9] 215–16 (1940). M.V.C.

Protective linings as a means for prolonging life of refractory products. R. T. MAKHL. *Keram. Sbornik*, **1939**, No. 4, pp. 11–24.—M. discusses (1) properties required of protective linings, (2) causes of destruction of refractory masonry, (3) composition of linings, and (4) methods of testing protective linings. M.V.C.

Refractoriness of silica and of its separate modifications. P. S. MAMYKIN AND V. V. SAPAROV. *Uralskaya Metallurgiya*, **1940**, No. 10, p. 22.—The authors reached the following conclusions: (1) The refractoriness of silica depends on the firing temperature; it reaches a maximum at 1280°C. and diminishes considerably at 1410°C. (2) The granulometric composition of the silica charge does not have a decisive influence on the refractoriness of silica brick. (3) Of the two raw materials used, quartz and crystalline quartzite, the latter is preferred. Crystalline quartzite fired at a low temperature produces a silica brick with a more compact and durable structure. (4) Silica brick fired at a temperature of 1280°C., compared with that fired at normal temperature, has a higher specific gravity and density and a lower porosity. The increase of the refractoriness of silica brick is due to the smaller glass content and the smaller thermal expansion coefficient of quartz in comparison with cristobalite. (5) Silica brick boiled in resin (of coal) well dehydrated possesses a higher refractoriness than normal silica. (6) In zonal brick, the cristobalite zone possesses the highest refractoriness. B.E.K.

Refractory block from Saar slate clay. ADOLF MÖSER. *Feuerungstechnik*, **28** [6] 126–31 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 1342.—Experiments were made on the manufacture of refractory block from raw slate clay from the Saar. The method of preparing the clay and the batch compositions are described. A refractory block could be obtained only when this raw material was used alone. Saar clay has a lower alumina content and lower refractoriness than Bohemian slate clay, but its resistance to deformation under load is good. If the methods of preparing the Saar clay were improved, high-grade grog block might also be made from it. M.V.C.

Refractory selection for petroleum cracking furnaces. M. G. VAN VOORHIS. *Nat. Petroleum News*, **30** [4] R19–24 (1938); *Brit. Chem. & Phys. Abs.–B*, **57** [6] 652 (1938).—The analyses and properties of various types of refractory brick are given, and their resistance to attack by CO, SO_2, H_2, etc., is discussed. Diatomaceous earth and crushed firebrick, etc., commonly employed as a backing to the brick, are being replaced by insulating refractory brick consisting chiefly of kaolinite.

Selection of durable crucibles with a definite gas permeability and the development of production methods for their manufacture. R. ROZENBERG. *Keram. Sbornik*, **1939**, No. 1 (2), pp. 56–57.—All data showed that, with an initial firing at a high temperature, gas permeability of the body increases. The mechanical strength also increases. The addition of talc to the mix is recommended. Such bodies are mechanically strong and durable; their firing temperature ranges from 1200° to 1250°. M.V.C.

Service of forsterite brick in the open-hearth furnace. P. EGOROV. *Stal*, **1940**, No. 7, pp. 47–48.—Forsterite brick is used for the back walls of open-hearth furnaces. These brick withstand about 274 fusions, while silica brick withstand only about 50 to 75 fusions. During this period, the thickness of the brickwork decreases from 500 to 100 or 150 mm. Forsterite brickwork should be made from the dry powder. It is not permissible to pour the silica solution over the joints, because this transforms the forsterite into a doughy formless mass. To prevent destruction it is necessary to separate the forsterite from silica brick by chromite-magnesite refractories. The pillars of the front walls and the angles of the "Venturi" of open-hearth furnaces are made from forsterite refractories. The forsterite did not cleave but became friable on cutting. B.E.K.

Service of forsterite refractories in steel-melting furnaces. A. BEREZHNOĬ AND V. GULYAEV. *Stal*, **1940**, No. 8, pp. 18–27.—Like magnesite, forsterite refractories absorb iron oxides from the melting space intensively and absorb other oxides less intensively. The wear of forsterite results almost wholly from cleaving. Forsterite brick do not fuse even with the addition of a flux. The cleaving of forsterite apparently results chiefly from the additional sintering of zones saturated with a flux and from the absorption, by ferrites crystallized into forsterite grains, of the iron oxides; this increases the inhomogeneity of crystals and increases internal strains. Forsterite is not subjected to intensive corrosion by slags and can be successfully used in place of magnesite and silica brick for inclined back walls of steel-melting furnaces which are above the slag level and for the back walls of open-hearth furnaces. See "Large scale . . . ," *Ceram. Abs.*, **20** [1] 18 (1941). B.E.K.

Silica brick and salt attack. G. E. FOXWELL. *Gas Jour.*, **218**, 803–804 (1937); *Chem. Abs.*, **32**, 3925 (1938).—No alkali was found to have combined with the material of a brick (containing 93% SiO_2) which had withstood coke-oven gases for 2 years, whereas brick containing only 80% SiO_2 failed in 7 months. Kaolin, quartz, tridymite, and cristobalite were rapidly attacked by fused NaCl.

Silica brick in vertical limekilns. ANON. *Cement & Lime Manuf.*, **11**, 257–59 (1938); *Brit. Chem. & Phys. Abs.–B*, **58** [3] 264 (1939).—The requirements for the refractory lining of vertical limekilns are discussed, and it is concluded that SiO_2 brick bonded with 2.5 to 3% of CaO would be suitable. With such brick additional insulation, e.g., by means of diatomaceous brick, would be necessary.

Slagging of refractories. G. E. FOXWELL. *Gas Jour.*, **219**, 606, 609 (1937); *Brit. Chem. & Phys. Abs.–B*, **56**, 1206 (1937).—The penetration and the dissolution of refractory materials by slag are considered from the viewpoint of physical and physicochemical principles.

Stability of floors of basic Martin furnaces in the working of materials containing vanadium. A. I. PASSTUKHOV, P. Y. MANSHOSS, AND K. M. PETROV. *Uralskaya Metallurgiya*, **1939**, No. 10–11, pp. 18–26; abstracted in *Chem. Zentr.*, **1940, II**, 809.—The process of smelting slags containing vanadium has no specific effect on the stability of bottoms of Martin furnaces. The chief cause of the corrosion of the furnace lining is the frequently unnecessarily long smelting time for masses with constantly increasing alkalinity; the slags become so viscous that it is difficult to remove them from the furnace bottom, and bonding cement and periclase are dissolved out of the refractory by iron oxide, leaving the easily fusible minerals. Measures for preventing this disintegration are described. M.V.C.

Stability of refractory materials containing silica and alumina to corrosion by Liburnian coal ash. GUISEPPE TRUCCO. *Calore*, **13**, 74–77 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 1066.—The resistance of this refractory block to corrosion by coal ash was not noticeably changed by varying the Al_2O_3 content, but the use of a composition of a definite grain size and shaping under high pressure while the blocks are half dry brought an improvement. The use of an Italian kaolin (of Laconi) was approved. M.V.C.

Talc-magnesite refractory. I. L. MOVSHEVICH. *Vestnik Inzhenerov & Tekh.*, p. 300 (May, 1938).—The Ukrainian Research Institute of Refractories has prepared a new forsterite (talc-magnesite) refractory for the roofs of open-hearth furnaces. The chemical composition, the process of preparation, and the results of tests are described. See *Ceram. Abs.*, **18** [5] 130 (1939). B.E.K.

Unfired chrome-magnesite brick. ANON. *Novosti Tekhniki*, **1940**, No. 7–8, p. 71.—The composition, process of preparation, and physical and technical properties of this brick are described. Unfired chrome-magnesite brick are used simultaneously with fired chrome-magnesite brick in major repairs of the back walls of open-hearth furnaces. B.E.K.

Use of artificial magnesite clay for lining the walls of the Martin furnaces. L. GIRSHMAN. *Novosti Tekhniki*, **1938**, No. 8, p. 5; *Chem. Abs.*, **32**, 6818 (1938).—Calcined magnesite (800°) was mixed with an equal volume of boiling water in the ball mill at 80° to 90°. After 1.5 to 2 hr., boiling water was added in the amount necessary to maintain a thin mash consistency. The clay is considered ready for use when a sample in the form of a cylinder (diameter 8 mm.) can be bent to a 10-mm. radius without

cracking. The duration of the clay preparation varied from 12 to 24 hr., depending on the initial material and temperature of the mass during the milling operation. The process can be cut in half by adding a small amount of some adsorbing substances (0.003% of sugar). The clay can be used without any admixture.

Use and maintenance of refractories in carbonizing industries. H. E. OLIVER. *Gas World*, **36**, 36–37 (1937); *Brit. Chem. & Phys. Abs.-B*, **56**, 241 (1937).—Advice is given for the handling of gas and coke-oven settings, with special reference to SiO_2 materials.

Washing of aluminate residue. ZIRO KOZIMA. *Waseda Applied Chem. Soc. Bull.*, **15** [3] 1–6 (in English, 40) (1938); *Chem. Abs.*, **33**, 5605 (1939).—In the wet preparation of Al_2O_3, the residue left after treatment of the bauxite with NaOH was washed with a volume of water equal to half the volume of aluminate solution. With this method of washing, about 97% of the Al_2O_3 in the residue was recovered.

PATENTS

Blast-furnace construction. A. J. BOYNTON (H. A. Brassert & Co.). U. S. 2,236,991, April 1, 1941 (Aug. 5, 1939).

Cellulated clay product and method of producing. W. G. FRANCE (G. A. Bole). U. S. 2,235,881, March 25, 1941 (April 9, 1936).—A cellular refractory ceramic product produced from a clay slurry which has been foamed, gelled, dried, and fired, wherein the foaming and gel-producing agents with the exception of alumina are removed from the final product, the clay being the major constituent of the product.

Furnace wall structure. MICHAEL LIPTAK. U. S. 2,238,122, April 15, 1941 (Jan. 20, 1939).

Insulating refractories and method of making. TITANIUM ALLOY MFG. CO. Brit. 533,910, March 5, 1941 (April 26, 1938).

Making basic refractories. M. Y. SEATON AND H. H. HARTZELL (Basic Dolomite, Inc.). U. S. 2,238,428, April 15, 1941 (May 23, 1935; May 20, 1938).—A process of making magnesia refractories of high structural strength and great refractoriness comprises heating magnesia with silica and lime in sufficient proportion to form a eutectic of monticellite with crystallization of the magnesia as periclase, cooling, comminuting, mixing with enough fine material containing CaO to convert the monticellite into calcium silicate, and reheating to effect this change and produce a hard solid matrix of dicalcium silicate enclosing and bonding the crystallized periclase.

Open-hearth furnace roof. H. S. ROBERTSON (Harbison-Walker Refractories Co.). U. S. 2,236,920, April 1, 1941 (Feb. 10, 1939).

Treating aluminous material to produce alumina. C. G. FINK AND V. S. DE MARCHI. U. S. 2,238,103, April 15, 1941 (March 8, 1938).—A process of purifying aluminous material comprises treating aluminous material containing more than about 15% Fe_2O_3 together with other impurities including TiO_2 and SiO_2 with an amount of at least one sulfur-bearing material selected from the group consisting of elemental sulfur, iron pyrite, alkali metal sulfide and polysulfide, and hydrogen sulfide in excess of the amount required to sulfidize the iron oxide to sulfidize a major portion of the impurities and to form sulfidized aluminous material substantially devoid of sulfur compounds of aluminum, reacting the sulfidized material with chlorine to form chlorides of the iron and other impurities, and separating the chlorides from the nonsulfidized alumina whereby alumina of commercial purity is obtained.

Terra Cotta

Complete removal of dust achieved in Cambridge Tile Mfg. Co. press room. ANON. *Ceram. Ind.*, **35** [5] 59–60 (1940).—At the Cambridge Tile Mfg. Co., Cincinnati, Ohio, dust is removed by suction hoods on each press which remove dust blown across the bed by compressed air. The presses are fitted with automatic thickness gauges. Wall tile is matched under a mixture of frosted white and mercury vapor blue lighting. Illustrated. A.F.M.

Glazing sintered bodies. Z. I. GLUSHANOK. *Keram. Sbornik*, **1939**, No. 1 (2), pp. 54–56.—The body is immersed in the glaze. The best thickening agents are sulfuric acid and ammonium carbonate. Electrolytes should be added during the grinding of the glaze. M.V.C.

SEPARATE PUBLICATION

Earthen Floor and Wall Tile. *U. S. Tariff Comm. Rept.*, No. 141, Second Series (1941). Supt. of Documents, Govt. Printing Office, Washington, D. C. 158 pp., 14 illustrations, 11 charts and maps. Price 25¢.—An economic survey of the floor and wall tile industry in the U. S. and other important producing countries is presented. It deals mainly with ceramic or fired clay tile, which are the most important kinds of earthen tile imported into the U. S. The report covers such economic aspects as the effects of tariffs on the floor and wall tile trade, problems in marketing (including competition from substitute materials), production costs, international trade in tile, and various phases of competition. Attention is also given to the classification of tile and the processes of manufacture.

Many countries produce floor and wall tile, and production in the U. S. is only a small part of the world's total. Highly industrialized countries usually make a complete line of modern tile, while others produce only crude floor tile or specialize in the manufacture of certain types. Most of the international trade in tile is confined to the more highly developed types such as decorative glazed tile. From 1926 to 1929, when building operations were very active, U. S. production of floor and wall tile averaged $28,000,000 annually, while average imports of $1,200,000 were three times as great as the value of exports in the same years. In 1939, domestic production was valued at $17,200,000, compared with imports and exports in that year of $21,000 and $268,000, respectively. These matters are discussed in detail, together with the effects which reductions in the rates of duty on these tile in recent trade agreements have had on the level of imports. Statistical data are given in the appendixes.

PATENTS

Ceramic pot. H. T. RITTER. U. S. 2,238,781, April 15, 1941 (Aug. 3, 1939).

Color control of ceramic products. J. McM. COOLEY (National Fireproofing Corp.). U. S. 2,237,478, April 8, 1941 (Oct. 3, 1939).—A method of applying a salt glaze to masonry facing materials comprises placing the materials on the floor of the kiln in spaced relation to expose the surface of the material to the atmosphere of the kiln, subjecting the articles to a firing temperature to a degree of desired vitrification, then charging the kiln atmosphere with sodium chloride vapor to form a soda-alumina-silica glass surface on the material, exhausting the sodium chloride vapor from the kiln chamber by natural draft after firing has been discontinued, and introducing cooling air into the kiln chamber through the stack flue and kiln bottom at a proper rate to lower the temperature of the articles so that the desired colors will be produced.

Flowerpot. H. T. RITTER. U. S. 2,238,132, April 15, 1941 (Feb. 15, 1939).

Whiteware

American dinnerware compared with imports: Bone china chips more readily than American vitreous ware. ARTHUR S. WATTS. *Ceram. Ind.*, **35** [6] 38 (1940).—Foreign and domestic dinnerware are compared. Bone china chips with about the same degree of use as vitrified ware, such as Belleek china and European porcelain, and definitely more readily than American vitreous china of the same thickness of edge. Bone china seems to have a greater tendency to crack under abrupt temperature change than any of the vitreous ware just mentioned. Swedish bone china will give superior service to most English bone china. The glaze on English bone china is softer and more easily scratched and scarred than that of the American vitreous china or the European porcelain. **Domestic china lines superior to English bone china.** ANON. *Ibid.*, pp. 38–39.—Repeated efforts to replace American hotel china with English bone china have all failed, due largely to the excessive glaze wear on English bone china under institutional conditions. **American china 25% stronger than imported ware.** D. W. SCAMMELL. *Ibid.*, p. 39.—Most American-made china is approximately 25% stronger than the foreign merchandise. **American glazes are as good as English glazes.** ANON. *Ibid.*, pp. 39, 56.—In an interview, Kennard L. Wedgwood states that there is no foundation for the belief that the glaze on English bone china lasts longer and is more resistant to crazing than American glazes. Illustrated. A.F.M.

Ceramic gas filters. L. A. VIKHIREV. *Keram. Sbornik*, **1940**, No. 7, pp. 42–44.—The problem of producing porous, mechanically strong filters with a high gas permeability has been solved. Bentonite of Oglalinkil deposits is an excellent bond for mullite grog products. It produces porous products with high mechanical strength. To increase gas permeability, sintered grog should be introduced into the mix. The finer the grain size of the grog, the greater is the mechanical strength and the smaller are the pores. M.V.C.

Comparative tests on whiteware glazes: III, Effect of sulfur dioxide on whiteware glazes containing lead and boron. W. STEGER. *Ber. Deut. Keram. Ges.*, **21** [6] 228–37 (1940).—Whiteware glazes were tested in a glost firing to determine their resistance to moisture containing 20% sulfur dioxide. Their composition was as follows: lead oxide 11.1 to 47.1, alkali oxides (K_2O and Na_2O) 0 to 12.9, calcium oxide 1.3 to 9.0, aluminum oxide 4.0 to 11.0, silica 35.7 to 55.8, and boric acid 4.5 to 15.0%. Glazes with the following composition are resistant to furnace gases containing sulfur: 17 to 20 lead oxide, 3 to 6 alkali oxides (potassium and sodium oxides), 4 to 6 calcium oxide, 4 to 8 aluminum oxide, 36 to 54 silica, and 5 to 12% boric acid. It is fundamentally necessary to keep the content of alkali oxides and calcium oxide low; the silica content may be slight (36 to 38%), and the boric acid need not exceed 12%. If the glaze is specially rich in alkali, the boric acid must be increased to above 12%. Glazes rich in lime may perhaps be made resistant to furnace gases containing sulfur by the introduction of zinc oxide. If the glazes are fired in a completely dry mixture of nitrogen and 2% sulfur dioxide, they are not injured as much as when oxygen and water vapor are present. For glazes which are not injured in appearance even under the latter conditions, firing in the nitrogen-sulfur dioxide mixture widens the range of fusion. When glazes have been glost fired in the stream of air, contact with damp air and sulfur dioxide causes surface changes such as dullness, cloudiness, separation of salts, or crystal skeletons. For Part II see *Ceram. Abs.*, **20** [3] 72 (1941); see also "Lead-free . . .," *ibid.*, [5] 120. W.H.H.

Compositions and properties of some high-titania ceramics. LOUIS NAVIAS. *Jour. Amer. Ceram. Soc.*, **24** [5] 148–55 (1941).—12 references, 4 figures.

Effect of zirconium silicate additions on abrasion resistance and various properties of several glazes. C. H. COMMONS, JR. *Jour. Amer. Ceram. Soc.*, **24** [5] 145–47 (1941).—1 reference, 1 figure.

Eutectic fluxes in semivitreous and vitreous whiteware bodies. C. R. AUSTIN AND S. J. BROOKS. *Jour. Amer. Ceram. Soc.*, **24** [5] 155–59 (1941).—3 references, 4 figures.

Investigating pegmatites of the Peredatochnaya station and their use for high-voltage porcelain. V. T. POPOVA. *Keram. Sbornik*, **1940**, No. 8, pp. 32–36.—These pegmatites contain from 25 to 30% quartz with an Fe_2O_3 content of 0.35 to 0.50%. They can be used in the production of high-voltage porcelain ware. Porcelain bodies made from them have a dark color with a number of small spots. These pegmatites may also be used as flux in the production of bodies whose appearance is not important. M.V.C.

Making insulators is a mud-pie job. ANON. *Popular Sci. Monthly*, **138** [3] 118–19 (1941).—Photographs show how Westinghouse makes electrical insulators at its Derry, Pa., plant. A.P.

Manufacture of thin-walled permeable ceramic bodies. R. T. MAKHL. *Keram. Sbornik*, **1939**, No. 2 (3), pp. 61–66.—The most difficult problem in the production of thin-walled permeable bodies is to insure a sufficient body strength and to obtain the required permeability. The introduction of agents which burn out does not insure a permeable body; they produce either low mechanical strength (low firing temperature) and low permeability or high mechanical strength (high firing temperature) and low permeability. The introduction of grog or kaolin has little effect on permeability. Alumina increases the permeability of bodies but lowers their mechanical strength. Melted magnesite and magnesium carbonate have a favorable effect on the permeability of the body. M.V.C.

Resistance to bending by shock and transparency of porcelain. LUDWIG STUCKERT AND OSKAR PAUL. *Ber. Deut. Keram. Ges.*, **21** [4] 150–67; [5] 171–200 (1940).—Porcelain bodies I to IV, with kaolin increasing from 40 to 65%, were tested for resistance to bending by shock and for transparency. Bodies I to VI, in the form of standard round rods 15 mm. in diameter, were tested by blows from a pendulum, and test plates of the bodies 10 x 15 x 3 mm. were tested in the Dynstat apparatus to determine the bending caused by blows and the bending strength. This apparatus, built by Schopper, can be used for dynamic or static bending tests. The pendulum was specially designed and built for this investigation. The Dynstat apparatus was tested for its suitability for testing the bending strength of porcelain under shock. The results of the bending strength tests are presented both graphically and in tables, and their degree of scattering is indicated. An attempt was made to find the cause of this scattering by microscopic examination of thin slices, and it was found that the lack of homogeneity in the glass phase of the porcelain was probably responsible. Bending-strength tests also showed that with increase in kaolin content there was a slight rise in the curve, which reached a maximum between 50 and 60% kaolin. Bending tests with body I (50% kaolin), in the form of test plates varying in particle size (quartz and feldspar) showed a clear maximum at a particle size of 10 to 25 μ and a decrease in strength with further increase in particle size. The static resistance to bending of the body increased steadily with increase in the kaolin content. Transparency measurements were made on the same bodies by the step photometer, and the standard plate was determined. The transparency of the porcelain, within certain limits of thickness (less than 1.9 mm.), decreased with increasing thickness according to a law analogous with the logarithmic law of Lambert-Beer'schen. The transparency of bodies I to VI decreased with increasing kaolin. The curves show clearly the superiority of hard porcelain bodies over technical porcelains and typical soft porcelains. With varying particle size of quartz and feldspar for body I, an improvement in transparency was found with a decrease in particle size. Maximum transparency was found with a particle size of quartz and feldspar of 10 to 25 μ. The absolute transparency of a standard por-

celain of 1.5 mm. thickness was determined by comparison with an opal glass which had been tested for turbidity and transparency and was found to be about 5% of the light falling upon it. W.H.H.

Sanitary porcelain. R. Rieke and K. Heinstein. *Ber. Deut. Keram. Ges.*, **21** [2] 62–78 (1940).—Tests were made on fragments A to I from various sources. The influence that the composition exerts on the characteristics of brand D is noteworthy. This body contains the largest amount of SiO_2 and shows the greatest strength. In the investigation of specific gravity and coefficient of thermal expansion, however, this body shows no increase in value in comparison with the others. That the free quartz has become partly dissolved in the feldspar glass can thus be assumed. Whether this transposition was brought about by longer firing or by a finer particle size of the quartz could not be determined. In the case of brands A and B, it can be assumed, on the basis of chemical analyses, that calcite was added as a flux. These two bodies show the greatest absorption and the lowest bending strength. The entire flux amounts to 6.8 or 6.7%, while that for the others amounts to only 5.8 to 6.1%. It might thus be assumed that bodies A and B would be the most dense. As this is not the case, the particle size of the quartz, the firing temperature, and other factors must be responsible for the undesirable characteristics. It cannot be assumed that the low strength of these two bodies is due to their high absorption, as body E with 0.5% absorption (2 hr. boiling) shows a considerably higher strength than body B with 0.6% absorption. The small amounts of calcite appear to have no effect on the coefficient of thermal expansion and the specific gravity. There is no apparent connection between the composition of the different bodies and their densities. This can be explained only by a difference in the firing temperatures and duration at the different plants; this should also explain why there is no relation between composition and coefficient of expansion. Brand G has the highest density and highest coefficient of expansion. Other factors such as the particle size of the raw materials, the differences in the clays, etc., influence the characteristics of the fired body so greatly that, in spite of the same composition, great differences can occur in the finished products. Tests on fragments of American hotel china, made for comparison, show that these bodies contain less kaolin and more quartz. The Fe_2O_3 and TiO_2 contents, which give the white firing color of the body, are lower compared with those of German bodies. From the lower TiO_2 content it can be concluded that no English ball clay is added, as this contains considerable TiO_2. Brand K has a surprisingly low feldspar content. With all American bodies (K to N), however, vitrification had progressed very far, as is shown by the very small absorption. All brands had densities of the same order of magnitude as the German bodies. The bending strength of the American bodies is generally 100 kgm. per cm.^{2} lower than that of the German bodies, the German values being between 600 and 700 kgm. per cm.^{2}. The coefficient of expansion was also measured for brand K; between 500° and 600°C. there is a very strong quartz effect. The coefficient of expansion is somewhat higher than that of the German fragments. This is also explained by the higher quartz content. W.H.H.

Substitute raw materials for the ceramic industry. Hans Lehmann. *Ber. Deut. Keram. Ges.*, **21** [2] 52–56 (1940).—The manufacture of synthetic materials is important in wartime. According to regulations, it is not permissible for the B_2O_3 content of ceramic glazes to be over 5%. Glazes previously developed for temperatures over Seger cone 2*a* have a B_2O_3 content of about 4% with a PbO content of 10 to 15%. They were prepared by mixing glazes free from boron or lead with customary glazes containing them. It is impossible to give a universally applicable formula for a new whiteware glaze, as the composition of the body quite markedly influences the glaze. Glazes showing the best results had the following molecular composition:

0.40 KNaO 0.20 BaO 0.8–0.16 MgO 0.8–0.16 CaO 0.8–0.16 ZnO	0.1–0.2 Al_2O_3	1.5–2.3 SiO_2

Barium compounds are, however, just as poisonous as lead compounds. It is therefore necessary to frit the barium compounds in every case to avoid the danger of starting a new occupational disease in the ceramic industry. It has long been a problem to obtain an opaque white glaze without using zinc oxide. The Auer Co. has recently done considerable work on zircon compounds for this purpose. These compounds were fairly successful for glazes with a melting temperature of about 1000°C., but for those with higher temperatures the solution of the zircon compounds jeopardized the opaqueness. The typical composition of glazes in which the zircon oxide is only slightly reduced is as follows:

0.35 ZnO 0.32 MgO 0.33 KNaO	0.35–0.45 Al_2O_3	3.0–3.8 SiO_2

Raw materials high in manganese are no longer available. For the preparation of bodies and glazes in which the content of SiO_2 and Al_2O_3 can be changed only to a limited extent, there are commercially available the so-called manganese slimes or similar by-products. The approximate composition of two of these products is as follows:

	Oasin Mn (%)	Toganit (%)
Loss on ignition	14	13
SiO_2	15	33
BaO	2	2
Fe_2O_3	33	5
Al_2O_3	5	8
MnO	27	33

A substitute for chromium ores has not yet been found. It is possible to prepare, from waste material, slag with the following composition: Cr_2O_3 about 6%, FeO about 8%, Al_2O_3 about 18%, SiO_2 28 to 30%, and MgO 31 to 32%. Practical tests are necessary to show how successfully this material can be used, in combination with gray-firing clay and suitable firing, to produce gray floor tile. An adequate supply of feldspar and of cotton for filter cloths is also necessary. W.H.H.

Utilize automatic handling methods in grinding-ball manufacture. Anon. *Ceram. Ind.*, **36** [2] 51–54 (1941).—A description is given of the plant of the McDanel Refractory Porcelain Co., Beaver Falls, Pa., manufacturers of grinding balls, mill-lining brick, protective tubing for wires, and porcelain boats for testing materials. Grinding balls are made in seven standard sizes from $^1/_2$ in. to 3 in. in diameter. The ingredients are ball clay, china clay, flint, feldspar (all air floated), and water amounting to 25 to 30% of the dry batch weight. After being mixed for 6 min., the moist body is formed into large balls, weighing 20 to 30 lb. each, which are passed through deairing and pugging chambers and then accurately formed. The 3-in. balls are dried for 3 days at 80°F. by a unit heater. The balls are fired to 2250°F. in a 24-ft. round downdraft periodic kiln fired with natural gas through six proportioning luminous flame burners placed only slightly above the inside floor level of the kiln. The kiln cycle is completed in 80 hr. Illustrated. A.F.M.

SEPARATE PUBLICATION

Properties of Clay Casting Slips. George A. Loomis. *Ohio State Univ. Eng. Expt. Sta. Circ.*, No. 39, 23 pp. (Jan., 1941).—The properties of clay casting slips were studied to determine a method of controlling them to give best results in the manufacture of cast products. Nine idealized bodies were made of 25% each of china clay, ball clay, flint, and feldspar. Various single clays of each type were used. These were blunged with water, and an electrolyte was added in increments until trial casts drained

properly and had the correct feel. The electrolyte was 60% "N" brand sodium silicate and 40% sodium carbonate. The particle size of each clay was run separately, using the Andreasen pipette. Other properties determined were (1) specific gravity, (2) consistency, (3) rate of cast, (4) drainage, (5) "feel" or degree of plasticity, (6) per cent of water retained by the cast, and (7) pH of slip. Changes in these properties at 0, 24, 48, and 96 hr. were also determined. With the proper plasticity, the per cent of a casting slip under 1μ in size is inversely proportional to the rate of cast. The per cent of electrolyte giving the proper plasticity varied from 0 to 0.16. The consistency rose slightly with age. The casting rate tended to decrease slightly with age, as did the per cent of water retained by the cast. The optimum pH values varied from 4.9 to 8.4 and decreased only slightly with age. These differences in optimum pH values were due to different pH values before the electrolyte was added. The pH determination should offer a reliable means of control of a casting slip of the same commercial body. This is contrary to accepted belief. 63 references. See *Jour. Amer. Ceram. Soc.*, **23** [6] 159–62 (1940). W.D.F.

PATENTS

Frangible tableware articles such as plates, saucers, etc. R. RATNER. Brit. 533,859, March 5, 1941 (Jan. 11, 1939).

Sagger pin boxing machine. RALPH BOWER, L. P. REESE, AND A. J. WAHL (Ralph Bower and A. J. Wahl). U. S. 2,236,890, April 1, 1941 (Dec. 21, 1936).

Spark plug. AC-SPHINX SPARKING PLUG CO., LTD., AND D. H. CORBIN. Brit. 533,658, March 5, 1941 (Oct. 5, 1939).

Spark plugs for internal-combustion engines. F. J. CLEVELAND (Bendix Aviation Corp.). Brit. 534,333, March 19, 1941 (June 23, 1939).

Sparking plugs. J. GABLER AND GRAYBLER CORP. (England), LTD. Brit. 533,700, March 5, 1941 (Nov. 15, 1939).

Sparking plugs for internal-combustion engines. LODGE PLUGS, LTD., AND B. HOPPS. Brit. 533,759, March 5, 1941 (Nov. 23, 1939). LODGE PLUGS, LTD., AND D. TURNER. Brit. 534,248, March 12, 1941 (Dec. 15, 1939).

Equipment and Apparatus

Annual review of materials and equipment. ANON. *Ceram. Ind.*, **36** [1] 31–44, 53–56 (1941).—A description is given of 92 pieces of equipment and materials, useful in pottery, glass, and enamel plants, which were introduced on the market in 1940. Illustrated. A.F.M.

Application of fan laws. G. A. HENDRICKSON. *Combustion*, **12** [1] 39–41 (1940).—Performance data for a fan or pump under given operating conditions are readily calculated, by the use of fan laws, from the manufacturer's constant-speed characteristic curve or equivalent data. To meet certain practical problems, a tabular statement of fan laws is given from which the combination applying to a particular problem can be chosen mechanically. The use of the table is illustrated. H.E.S.

Application of the Figurovskiĭ sedimentometer to the determination of the granulometric composition of abrasive materials. T. E. GOLBA. *Zavodskaya Lab.*, **9**, 1172–76 (1940).—The Figurovskiĭ sedimentometer is suitable for determining the granulometric composition of abrasives from 0 to 100μ and replaces the Andrezen-Wims and Robinson devices, accelerating the analysis fivefold. The accuracy of the analysis is within 2 to 3% and may be increased. P.B. & E.S.

Centrifugal slip casting. C. R. AUSTIN AND G. H. DUNCOMBE, JR. *Bull. Amer. Ceram. Soc.*, **20** [4] 113–16 (1941). —3 references, 2 figures.

Cuts working time 80% in making dies for ceramic parts. ANON. *Ceram. Ind.*, **35** [5] 47 (1940).—A new contour cutting machine which offers great time savings in the fabrication of dies for ceramics is described. Less skilled help is required than when the dies are made by broaching and milling. Illustrated. A.F.M.

Design and performance of an electron diffraction camera. J. E. RUEDY. *Rev. Sci. Instruments*, **11** [9] 292–95 (1940). H.E.S.

Determination of the granulometric composition of abrasive materials. T. E. GOLBA. *Zavodskaya Lab.*, **9**, 1053–55 (1940).—Recent methods of sedimentometric analysis are preferred to the Anderson-Wims and Robinson methods, the latter being unsatisfactory in several points. P.B. & E.S.

Determination of the moisture content of ceramic masses. S. MAKARIN. *Stroitel. Materialy*, **1938**, No. 3, pp. 21–23; *Chem. Abs.*, **34**, 866 (1940); see *Ceram. Abs.*, **19** [5] 120 (1940).

Device for measuring the extinction angle. HIDEO INUZUKA. *Amer. Mineralogist*, **25**, 735–37 (1940).—To measure the extinction angle more accurately, a photoelectric cell is used to collect the light from the microscope, and the output of a single stage amplifier is then run to a galvanometer. An objective with a power high enough so that the grain fills the field must be used. The position of the minimum galvanometer reading may be observed directly, or the angular position of the crystal against milliamperes may be plotted. W.D.F.

Dust collection needs correct hood design. J. G. LISKOW. *Nat. Safety News*, **42**, 52 (Aug., 1940).—A study of three types of operations, viz., foundry shakeouts, spray booths, and heating furnaces, showed the importance of having collector dust terminals properly hooded to provide efficient intake of dust and fumes. Three factors affecting proper operation of hoods include natural drafts, impact reflex action, and size of material being worked on. The best location of the hood is above and to one side of the operation, with curtains on the side and back to prevent eddy currents. Exhaust ducts should be taken from the plenum back of the louvers either upward, downward, or sidewise. Movable louvers were devised to meet variable conditions. One of the several types of movable louvered intake hoods is shown. It was used in experimental work and became the finally adopted design. F.S.M.

Electrical lubrication of dies of pug-mill brick presses. K. A. NOKHRATYAN AND P. D. GONCHAR. *Prom. Stroitel. Materialov*, **2** [8] 41–43 (1940). P.B. & E.S.

Electrically driven magnetically supported vacuum type ultracentrifuge. C. SKARSTROM AND J. W. BEAMS. *Rev. Sci. Instruments*, **11** [12] 398–403 (1940). H.E.S.

Equipment for the double variation method of refractive index determination: I, Improved stage cell. V. A. VIGFUSSON. *Amer. Mineralogist*, **25**, 763–65 (1940).—To eliminate the trapping of air bubbles and to reduce turbulence, a cell is made from two elliptical brass plates with holes in the center and cover glasses cemented over them. A thin cork gasket between the plates determines not only the thickness of the water compartment but also its shape. **II, Variable temperature control apparatus.** *Ibid.*, pp. 765–66.—This apparatus is for laboratories without hot water. One constant head device supplies cold water to the mixing valve, a second supplies cold water to the heater, and a third supplies hot water to the mixing valve. W.D.F.

Greater cast-ware output with automatic machine. ANON. *Ceram. Ind.*, **36** [3] 49–51 (1941).—An automatic casting machine which turns out 650 cosmetic containers per hour at the A. E. Hull Pottery Co., Crooksville, Ohio, is described. The basis of the casting system is a pair of synchronized chain conveyers, spaced about 4½ ft. apart, carrying between them metal racks about every 2 ft., each of which holds a gang of 9 plaster molds. The conveyer is encased for most of its length in a wooden housing which offers adequate insulation against loss of the heat intro-

duced from unit heaters and waste-heat ducts. The conveyer travels at a speed of 38 ft. per hr. at a top temperature of 170°F. The molds are filled and, after traveling about 50 min., are dumped; they are then broken and replaced on the racks being conveyed back to the filling position. Illustrated. A.F.M.

Instrument designed to record continuously the amount of dust in air. C. W. Biccard Jeppe and E. C. Halliday. *Jour. Chem. Met. Mining Soc. S. Africa*, **38**, 75–80 (1937).—Dust concentration is measured continuously by photoelectric cells connected through a Wheatstone bridge to a string recording galvanometer. The variation of the galvanometer reading with dust density is almost linear. The limit of sensitivity is about 50 particles per cc. The apparatus is described. See "Discussion . . . ," *Ceram. Abs.*, **17** [9] 318 (1938). A.H.E.

Measurement of temperature. E. C. Rollason. *Metallurgia*, **18** [Oct.] 203–205; **19** [Nov.] 15–16 (1938); *Jour. Iron & Steel Inst.* [London], **139** [1] 280A (1939).—R. explains the theory of thermocouples for temperature measurement, describes the characteristics of certain thermocouple wires, the millivoltmeter, and the potentiometer, and discusses the errors which may arise when using them. He also explains the principles of radiation and optical pyrometers.

Method and instrument for the measurement of very small amounts of heat and changes of temperature. S. Zamenhof. *Rev. Sci. Instruments*, **11** [4] 123–25 (1940). H.E.S.

Microscopic examination of loose and porous mineral building materials. V. N. Dominikovskii. *Zavodskaya Lab.*, **7**, 1073–76 (1938); *Chem. Abs.*, **33**, 1466 (1939).—Known methods of microscopic examination and classification of cement, sands, clays, and other granular building materials are discussed. See "Necessity . . . ," this issue, p. 142.

New heatproof Fe-Cr-Al alloys of high resistance. I. Kornilov. *Stal*, **1940**, No. 5, pp. 59–69.—K. prepared the following three kinds of high-resistance alloys for electrical resistance furnaces: Alloy No. 1, of the composition Fe 63.14, Cr 25.94, Al 8.5, Si 0.55, and C 0.02%, has a working temperature of 1000°C., and its life is about 2000 hr. Alloy No. 2, of the composition Fe 63.14, Cr 31.40, Al 5.4, Si 0.65, and C 0.03% (in ribbon and wire), has a working temperature of 1200° to 1250° and is used as a substitute for the platinum in electrical resistance furnaces; a refractory material neutral to this alloy at high temperatures should be used. Alloy No. 3, containing 50 to 55% Fe, has a working temperature of 1300° to 1400°C. and can be used as a substitute for the Globar elements in electric furnaces. B.E.K.

Preservation of filter-press fabrics by antiseptics. V. V. Sukachev. *Prom. Stroitel. Materialov*, **2** [8] 48–52 (1940).—Copper tannates have been found to be the most efficient. Investigations on solvent naphtha proved it to have good preserving properties. P.B. & E.S.

Reference values for temperature, pressure, and humidity. P. L. Bellaschi and P. H. McAuley. *Elec. Eng.*, **59**, 669–75 (1940); *Chem. Abs.*, **35**, 1271 (1941).—Reference values are frequently not conducive to easy comparisons of testing data. A more rational basis is advocated. It seems reasonable to minimize the number and the ranges of the reference conditions.

Tunnel drier refinements. T. W. Garve. *Bull. Amer. Ceram. Soc.*, **20** [4] 117–18 (1941).—4 figures.

Use of liquid surfaces as standards of specular gloss. Dwight G. Moore and Richard S. Hunter. *Jour. Amer. Ceram. Soc.*, **24** [5] 167–70 (1941).—9 references, 1 figure.

Use of the Wulff net in mineral determination with the universal stage. John C. Haff. *Amer. Mineralogist*, **25**, 689–707 (1940).—The Wulff net is a convenient and valuable aid in plotting data obtained from universal stage measurements. The necessary procedures are given here. W.D.F.

X-ray apparatus for determining the coarse structure of industrial materials. J. E. de Graaf. *Philips Tech. Rundschau*, **5**, 69–74 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 1062.—Insulation and other factors in the construction of X-ray apparatus for examining the structure of industrial materials are discussed. M.V.C.

PATENTS

Manufacture of ceramic ware. N. S. Garbisch. Brit. 534,673, March 26, 1941 (Dec. 16, 1938).

Material control means for spray appliances. H. L. Striegel (Binks Mfg. Co.). U. S. 2,236,551, April 1, 1941 (April 6, 1939).

Material disintegrating and air classifying system. W. B. Prouty. U. S. 2,236,548, April 1, 1941 (Nov. 6, 1937).

Molded brick manufacturing apparatus. Viktor Ehrenhaft. Can. 395,671, April 1, 1941 (July 26, 1939). G.M.H.

Optical pyrometer. H. W. Russell (Battelle Memorial Inst.). U. S. 2,237,713, April 8, 1941 (Sept. 20, 1938).

Sandblast gun. C. E. Pletcher. Can. 394,925, March 4, 1941 (April 16, 1938; in U. S. April 17, 1937). G.M.H.

Kilns, Furnaces, Fuels, and Combustion

Conditions of firing of sanitary ware. S. Listov. *Keram. Sbornik*, **1939**, No. 1 (2), pp. 58–60.—To obtain a white body, a 5-hr. firing in an oxidizing atmosphere at a temperature of 900° to 1000° (depending on the composition) is necessary. The temperature should be increased gradually to avoid warping. The finishing temperature ranges from 1280° to 1350°. The atmosphere should be weakly reducing to weakly oxidizing. The interval of 550° to 600° is the most dangerous cooling interval; cooling should be very gradual. M.V.C.

Constructive improvements in porcelain periodic kilns and frit furnaces. Adolf Langhof. *Ber. Deut. Keram. Ges.*, **21** [4] 141–44 (1940).—Older kilns are being rebuilt. A plant of 6 muffle ovens which were inadequate, employing 18 smelters and 18 helpers, produced 8700 kgm. of porcelain per day using 9000 kgm. of coal. These ovens were replaced by a double tunnel muffle oven which required only 3 smelters and 12 helpers; 10,200 kgm. of porcelain were produced per day using 2700 kgm. of coal. The entire cost of the new installation, including reconstruction of the building, was saved in one year as a result of the reduction in cost of operation. W.H.H.

Development of pottery firing. H. S. Walter. *Jour. Record Trans. Junior Inst. Engrs.*, **49**, 543 (1938–39).—W. reviews the fundamentals of pottery firing and describes the various types of kilns used. B.C.R.

Economical firing in ceramics. A. Möser. *Keram. Rundschau*, **48** [2] 9–12; [3] 22–24; [4] 31–34; [6] 48–50; [8] 65–67 (1940).—M. discusses the thermal processes in the firing and drying of ceramic products and the influence of the type and construction of the furnace on the economy of the thermal processes. The composition and the heating values of solid fuels are given in tables. Curves show the effect of preheated air on the combustion temperature with varying amounts of excess air. The principal requirement of fuel for ceramic purposes is that the velocity of combustion in the combustion chamber be such that the interior of the furnace and the material in it are heated with the maximum temperature increase compatible with the nature of the material. The temperature differences occurring in the furnace thus remain within the limits permissible for satisfactory production. Lignites are among the most valuable fuels for ceramic firing as they give sufficiently high temperatures, have a low grate charge because of their loose ashes, are quick burning due to their low inflammation point, and give a mild flame because of

their high content of volatile constituents. Bituminous coals are suitable as fuels only if they are rich in gas and give a loose coke. The efficiency and proper combustion for producing a satisfactory fired piece depend largely on the type and arrangement of the grate; the various types of grates are reviewed. The heat balance of the different types is, in general, useful heat 20%, losses by rusting up to 10%, waste-gas losses 30 to 40%, and radiation losses 30 to 40%. To increase the economy of furnaces, the last two sources of loss must be considered in particular. Modern constructions are described. M.H.

Electricity for firing ceramic products. A. I. Avgustinik, G. L. Krever, and V. M. D'akonov. *Keram. Sbornik*, 1939, No. 4, pp. 1–11.—The use of electric furnaces for firing ceramic products is discussed, and their advantages and disadvantages are given. M.V.C.

Fires twelve artware pieces to cone 10 for penny's worth of natural gas. Anon. *Ceram. Ind.*, **36** [2] 38–39 (1941).—A tunnel kiln at the Grindley Artware Mfg. Co., Sebring, Ohio, is 48 ft. long and has a setting space $14^1/_2$ in. wide and $28^1/_2$ in. high; it holds about two-thirds as much ware as the usual 150-ft. pottery bisque kiln. Hourly gas consumption is 400 cu. ft. costing 21¢, and the power cost is $5^1/_2$¢ per hr. The kiln has many breaks and fans for efficient thermal control. Illustrated. A.F.M.

Heat transfer. A. Blackie. *Fuel Econ. Rev.*, **17**, 72–78 (1938); *Jour. Iron & Steel Inst.* [London], **139** [1] 6A (1939).—B. discusses, under the headings of conduction, convection, and radiation, the important principles of heat transfer as they affect many problems arising from day to day in industry.

Improved continuous brick firing. A. G. Arend. *Fuel Economist*, **14**, 309–10 (1938); *Chem. Abs.*, **33**, 5616 (1939).—High-pressure but not superheated steam is used for drying. The brick are then fed into the kiln by special Cr-steel chain conveyer belts. The conveyers travel slowly and are tiered one above another; each is raked independently by a pulverized-fuel burner.

Progress in the design of electric furnaces in the ceramic industry. E. Schirm. *Keram. Rundschau*, **48** [9] 74–76; [12] 102–103 (1940).—Recent developments are reviewed. Formerly, tunnel kilns only were heated electrically; batch furnaces are now also heated in this way. This was made economical by reducing the stored heat by the use of heat-insulating brick which were lined on the inside with a mechanically stronger refractory for the support of the heating elements. The outside consisted of a metallic (steel sheet) mantle. S. describes methods of building the furnace to avoid cracking and breaking apart due to the continuous expansion and contraction of materials of different heat expansion, arrangement of the heating elements, temperature control in the different heating zones of tunnel kilns, and the various forms of brick used. M.H.

Recent developments in the utilization of carbon electrodes. A. F. Myrtsmov, V. D. Oshchepkov, Kh. Kadarmetov, and A. M. Polunin. *Kachestvennaya Stal*, **5** [12] 13–18 (1937).—The development of an electrode design is reported in which a short C electrode is attached to a water-cooled Fe electrode. Very satisfactory experimental results were obtained as a result of the better utilization of the C electrode when tested in 4 arc furnaces of 8- to 15-ton capacity. B.E.K.

Steelton plant burns coke breeze and anthracite on traveling-grate stokers. H. K. Miller. *Combustion*, **12** [1] 26–27 (1940).—Coke breeze and anthracite are burned together on a traveling-grate stoker with the anthracite forming the lower layer and the coke breeze the upper layer. Blast-furnace gas is also burned up to the limit of its availiability, and the speed of the stoker is automatically controlled to make up the deficiency. Initial operation indicates an efficiency of 79.6% with this arrangement, which measures up to the anticipated performance. H.E.S.

Swelling of sintered products because of varying water content. W. Kaufmann. *Ziegelwelt*, **71**, 170 (1940); abstracted in *Chem. Zentr.*, **1940**, II, 1197.—To prevent swelling, solidly compressed bodies (in which the water content may vary) must be fired in an oxidizing medium for a longer time before vitrifying. M.V.C.

Upkeep of continuous furnaces for tile and brick. J. Welter. *Rev. Matériaux Construction Trav. Publics*, No. 358, pp. 73–75B (1939).—W. gives general rules for the repairing and regular servicing of parts of continuous furnaces. The compositions of several refractory putties for repairing masonry subjected to temperatures from 800° to 1100° are also given. M.V.C.

Ventilation of Hoffman kilns. A. G. Meer. *Prom. Stroitel. Materialov*, **2** [8] 46–47 (1940).—A portable ventilation device for cooling the chambers of the kiln during the discharging process is described. P.B. & E.S.

SEPARATE PUBLICATION

Plans and Progress of Anthracite Research. A. W. Gauger and C. C. Wright. *Trans. Third Annual Anthracite Conference of Lehigh University*, 1940; reprinted in *Penna. State Coll. Mineral Ind. Expt. Sta. Tech. Paper*, No. 57. Price 25¢. V.D.F.

PATENT

Apparatus for use in the firing of pottery ware. J. Wedgwood & Sons, Ltd., and C. T. Wedgwood. Brit. 534,546, March 19, 1941 (Feb. 20, 1940).

Geology

Action of Zettlitz kaolin on heating studied by measuring the dielectric constant. W. de Keyser. *Ber. Deut. Keram. Ges.*, **21** [2] 29–51 (1940).—Several authors have followed the changes undergone by kaolin in heating by means of the index of refraction. The index of refraction is measured with ordinary light with a vibration number of about 10^{14}, while the dielectric constant is measured with X rays with the aid of electromagnetic waves having a frequency of 10^8. The dielectric constant appears to be more suitable for the purpose because it can be determined by waves of a much lower frequency. Stark's method for determining the dielectric constant was used. This consisted of mixing two liquids in varying proportions until the capacity of the cell filled with the mixture was the same whether or not the mixture contained the powder in suspension; it could then be said that the dielectric constant of the powder was the same as that of the liquid. The formula for kaolin is $2SiO_2 \cdot Al_2O_3 \cdot 1.75H_2O$ instead of $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$. After the water is driven off, metakaolin ($2SiO_2 \cdot Al_2O_3$) is formed. Between 800° and 830°C. the metakaolin decomposes. Between 850° and 910°C. decomposition continues and γ-Al_2O_3 is formed. Between 910° and 975°C. sillimanite is formed, and at higher temperatures mullite is formed. See "Formula. . . ," this issue, p. 154. W.H.H.

Barite deposit at Pessens near Rodez (Aveyron). J. Durand and E. Raguin. *Bull. Soc. Géol. France*, **8**, 755–64 (1938); *Chem. Abs.*, **34**, 60 (1940).—The deposit yielded 100,000 tons in the past 10 years. As extracted, the material contains 30% of clay and limestone. Borings show it to extend horizontally over about 50 acres at a shallow depth. Where worked it is 1 to 2 m. thick, beds of pure barite being intercalated in yellowish marly or siliceous (jasperoid) Liassic strata; the latter has resulted from silicification of a dolomitic limestone. Silicification was followed by introduction of the barite by hot solutions. The deposit is an extreme case of metasomatosis. More or less similar deposits are fairly common in the neighborhood, the barite in places being accompanied by sulfides, e.g., the deposit at St. Rome-de-Tarn contains sphalerite, galena, and chalcopyrite.

Cascade andesites of Oregon. Richard Bogue and Edwin T. Hodge. *Amer. Mineralogist*, **25**, 627–65 (1940).—A study of the Cascan formation of the Cascade

Mountains of Oregon is summarized. Several-thousand specimens were collected, and several-hundred thin sections were prepared. Over fifteen of the minerals present are discussed with regard to appearance, optical properties, origin, order of crystallization, and resorption. The minerals present occur in combinations which ordinarily define many different kinds of rocks; a study shows, however, that each was in process of attaining equilibrium but was frozen at different places along the route. Effects of magma contamination, resorption, reaction, and arrested stages were found. The original magma was a dacite, and it would ordinarily have all changed to an andesite made of pigeonite and labradorite. W.D.F.

Cause of the color of blue quartz of Charnockite of Southern India and the champion gneiss and other related rock of Mysore. N. JAYARAMAN. *Proc. Indian Acad. Sci.*, **9A,** 265–85 (1939); abstracted in *Chem. Zentr.*, **1940, II,** 1408.—When this quartz is heated to 300° the blue color disappears. Under a microscope and when light passes through it, this colored quartz has a brownish yellow turbidity which also disappears after heating. The turbidity is proportional to the intensity of the color. Colorless quartz does not have this turbidity. Needle-like inclusions of rutile are also present. The intensity of the coloring depends on the TiO_2 content, the effect of the rutile present being considered; the TiO_2 content is much greater than the rutile content. The turbidity is probably caused by the presence of a material containing TiO_2 in the colloidal state. M.V.C.

Chemical and mineralogical study of feldspars from mica pegmatites of Nellore, Madras. N. JAYARAMAN. *Proc. Indian Acad. Sci.*, **11A,** 116–37 (1940).—The feldspars may be classified as nonperthitic, perthite-microperthite, and microperthite. There is a mutual solubility, although to a limited extent, between the soda and potash feldspars and between soda feldspar and anorthite. The color of these feldspars is not schiller color but is due to an iron compound. A.P.S.

Cordierite-anthophyllite rocks associated with spinel-hypersthenites from Toodyay, Western Australia. REX T. PRIDER. *Geol. Mag.*, **77,** 364–82 (1940).—Cordierite-anthophyllite rock occurs as a xenolith in a granite gneiss. From a study including field relations, petrography, and chemical analyses, P. concludes that the cordierite-anthophyllite rock was derived from the spinel-hypersthene rock by the addition of silica and metamorphism, both being due to the intrusion of the granite. W.D.F.

Cristobalite in bentonite and fuller's earth. JOHN W. GRUNER. *Econ. Geol.*, **35** [7] 867–75 (1940).—Bentonites and fuller's earth may contain as much as 40% cristobalite, although none has been found in clays older than the Cretaceous. Although cristobalite is a common constituent of bentonitic clays, no satisfactory hypothesis can be advanced for its origin. See *Ceram. Abs.*, **20** [4] 102 (1941). B.C.R.

Crystallography of ulexite. JOSEPH MURDOCH. *Amer. Mineralogist*, **25,** 754–62 (1940).—Ulexite, $NaCaB_5O_9 \cdot 8H_2O$, was found in measurable crystals in the Suckow Borax Mine, Kramer District, San Bernardino County, California. It was triclinic, with many crystals flattened parallel to 100, giving a lathlike appearance. W.D.F.

Decomposition and alteration of feldspars and spodumene by water. LEE C. ARMSTRONG. *Amer. Mineralogist*, **25,** 810–20 (1940).—An investigation was made to determine the amount of decomposition of feldspars by prolonged grinding at room temperature and to determine whether a clay mineral could be produced by this method or whether a higher temperature was needed. Microcline and albite were ground 900 hr. in an agate mortar; kunzite was ground 400 hr. The suspensions produced were electrodialyzed, and it was found that all constituents of the minerals diffused through the membrane, i.e., they were all present as ions. The feldspars lost over 50% of their alkalis, and the kunzite lost 44% of the lithia. Chemical analysis of the fresh minerals and their decomposition products showed that the order of solution of the components of the feldspars was $CaO > Na_2O > K_2O > SiO_2 > Al_2O_3$. The decomposition products were hydrated, but dehydration curves showed that it was mainly adsorbed water. X-ray investigations showed that substantial amounts of the original minerals remained in the residues and that no new minerals were formed. When the residues were treated in a bomb at 300°C. with water present, quartz and probably kaolinite were formed. W.D.F.

Dehydration of pollucite. MICHAEL FLEISCHER AND C. J. KSANDA. *Amer. Mineralogist*, **25,** 666–72 (1940).—Pollucite showed practically no loss in weight under 300°, but it was completely dehydrated at 640°C. These values are not typical of a zeolite, but X-ray studies showed no change in the crystal lattice on dehydration. The refractive index dropped owing to the substitution of air for water in the mineral. Dehydrated pollucite did not pick up water at room temperatures, but it was partially rehydrated without decomposition in a bomb at 400° to 500°C. W.D.F.

Discovery of dumortierite on the banks of the Gava (South Fergana). V. I. POPOV AND A. L. VOROL'EV. *Razvedka Nedr*, **10** [2–3] 97–98 (1940); abstracted in *Chem. Zentr.*, **1940, II,** 1118.—On the banks of the Gava River (Usbekistan), a mineral was found which contained 41.69% SiO_2, 0.4 TiO_2, 50.44 Al_2O 0.09 Fe_2O_3, 0.08 FeO, traces of MgO, 4.19 B_2O_3, 0.6 SO_3, and 0.17 $K_2O + Na_2O$. Its density is 3.221. It is believed to be a quartz porphyry transformed by hydrothermal agents. Because of its high alumina and low iron and base content, this material should be highly refractory. M.V.C.

Druzhkovskiĭ clays and their technical standards. M. M. KUZMIN. *Keram. Sbornik*, **1940,** No. 7, pp. 11–25.—K. discusses deposits of Druzhkovskiĭ clays and their origin, mineralogical composition, classification, and ceramic properties. M.V.C.

Formation of cristobalite and quartz by heating vitreous silica under high pressure by means of explosives. A. MICHEL-LÉVY AND J. WYART. *Compt. Rend.*, **210** [22] 733–34 (1940).—During experiments on the crystallization of vitreous silica, quartz and cristobalite were obtained in a silver tube under pressures of 3000 to 4000 kgm. per cm.^{2} and at temperatures of 450° to 700°C.; tridymite was not obtained. Quartz was produced by the introduction of water and potash into the tube at 440°, 520°, 530°, 550°, and 720°; the heating period thus lasted between 4 and 13 days. An X-ray diagram shows that the quartz which crystallized at 720° had the appearance of vitreous pumice stone. Cristobalite was produced with the introduction of water only; a glass was obtained at 515° and cristobalite at 545° and 610° in 6 to 10 days. By replacing the Ag tube with a Cu tube, quartz could be produced with the introduction of water only, without alkali. Heating at 408° produced glass, at 450°, 517°, 525°, 545°, and 605° quartz, and at 720° and 730° a pumice of cristobalite; the heating time was 4 to 13 days. Cu has this mineralizing action for quartz between 450° and 650°C.; potash in the Ag tube has the same action between 440° and 720°C. M.H.

Formula of kaolinite. R. SCHWARZ. *Ber. Deut. Keram. Ges.*, **21** [4] 144–46 (1940).—According to W. de Keyser ("Action . . . ," this issue, p. 153), the formula for kaolinite should be $Al_2O_3 \cdot 2SiO_2 \cdot 1.75H_2O$. If an author wishes to have a new formula accepted, he must first prove the purity of his sample, but de Keyser has not done this. His conclusion that kaolin contains 12.5% of chemically bound water may imply that his test material contained 90% kaolinite and 10% of other materials which were water free. W.H.H.

Industrial minerals. SAMUEL H. DOLBEAR. *Eng. Mining Jour.*, **142** [2] 91–93 (1941).—D. reviews developments in nonmetallic minerals during 1940. W.D.F.

Investigation of the finest fractions of bentonite and clay soil with the universal electron microscope. M. v. ARDENNE, K. ENDELL, AND U. HOFMANN. *Ber. Deut. Keram. Ges.*, **21** [6] 209–27 (1940).—Electron microscope pictures of bentonite from the ultracentrifuge permit the recognition of plates with a thickness of only 1 mμ, which corresponds to an elementary layer of montmorillonite

crystal. The ratio of thickness to greatest length of kaolinite crystals should lie between 1:5 and 1:25, and that of bentonite, between 1:100 and 1:300. These plates confirm the conclusions drawn from X-ray investigations in regard to the structure of the montmorillonite crystals. Quartz particles as small as 0.5 micron were found, as was previously determined by W. Eitel and coworkers ("Ultramicroscopic . . . ," *Ceram. Abs.*, **18** [8] 222 (1939)). Opal particles 0.1 micron in diameter were found in Italian bentonite. The crystals of iron oxide and clay soil hydrate in the Brazilian coffee soil were also notably small (40 microns). A comparison of German and American bentonite showed that the German contained finer, more strongly roughened particles which facilitated an intimate fastening. In the American bentonite the plates were quite smooth, which made them suitable for film formation. Certain practical results were obtained in the application of the different bentonites as material in suspension, for flushing liquids for deep boring, synthetic foundry sands, and film formation. The application of the electron microscope test method to the finest fraction of soil and to the seldom investigated brick clay gave better knowledge of their water content and their transformation characteristics. W.H.H.

Iron compounds in kaolins and clays and their behavior on firing. R. Rieke and J. Plein. *Ber. Deut. Keram. Ges.*, **21** [7–8] 265–78 (1940).—Eleven samples of kaolin and clay were first examined to determine the total iron content and the ferric and ferrous iron contents separately. The content of FeO was then determined after an oxidizing firing at various temperatures, and the color was measured for seven of the samples. The content of FeO first decreased, due to oxidation (up to 900° to 1000°C.); at higher temperatures, with the passing of the iron into silicate combinations, FeO increased. Three of the kaolins and a hard porcelain body were fired in a regular porcelain kiln. The firing was oxidizing up to 1050°C. The FeO content again first decreased and at higher temperatures increased. Five clays rich in iron were fired in a porcelain kiln to Seger cone 16. After this reducing firing, a considerable part of the iron was present in the protoxide form, either as FeO silicate or partly as Fe_3O_4. A table gives the amounts of Fe_2O_3 obtained by shaking the three kaolins and the hard porcelain body for 1 hr. with 8% HCl after firing to various temperatures. A maximum amount of Fe_2O_3 was obtained at a temperature of 700° or 750°C. W.H.H.

Lauderdale County mineral resources. V. M. Foster and Thomas E. McCutcheon. *Mississippi State Geol. Survey Bull.*, **41**, 246 pp. (1940); *Chem. Abs.*, **35**, 712 (1941).—Chemical analyses and physical tests of a large number of clay samples are given. Some are suitable for use in ceramics, brick manufacture, etc.

Mineral dressing. A. M. Gaudin. *Eng. Mining Jour.*, **142** [2] 80–81 (1941).—Progress during 1940 is reviewed. W.D.F.

Occurrence of celestite in the phosphatic nodules of Utatur. N. Jayaraman and K. R. Krishnaswami. *Current Sci.*, **8** [12] 553 (1939).—Heretofore no significant deposits of strontium minerals were known to exist in India. The authors report the finding of a large source of strontium compounds in phosphatic nodules of which there are extensive deposits in the Utatur area, India. Crushed specimens of phosphatic nodules revealed the presence of a white platy mineral which filled the cracks in the nodule and appeared to have concentrated near the core. It could be easily loosened and isolated and comprised more than 3% (even 10% in exceptional cases) of the entire nodule. A chemical examination showed that the mineral consisted of approximately 93 strontium sulfate, 4 sulfate of calcium and barium, and 3% quartz. Celestite was also found in the gypsum beds in the same area. A.P.S.

Origin of some pegmatites of Newry, Maine. B. M. Shaub. *Amer. Mineralogist*, **25**, 673–88 (1940).—Four pegmatites occur 6½ miles south of Andover, Maine. The principal pegmatite shows a band of albite on the hanging wall and then a band of quartz with intergrown albite and muscovite. The succeeding bands are muscovite and albite. The repetition of albite belongs to a type of banding produced by a process of rhythmic fractional crystallization. The origin of these pegmatites is due to progressive fractionation of single injections of pegmatite magma. There is no evidence that any magma contained more than 5 to 10% water or that these pegmatites replaced earlier ones and no evidence of later hydrothermal solutions. W.D.F.

Physicochemical properties of Indian bentonites. N. C. Sen-Gupta. *Jour. Indian Chem. Soc.*, **15**, 559–65 (1938); *Chem. Abs.*, **33**, 3231 (1939).—The relation of chemical compositions, exchangeable bases, and base-binding capacities of seven natural Indian bentonites to their swelling and thixotropy was determined.

Physicochemical study of the nature of reactions occurring in kaolin on heating within the temperature range of porcelain firing (1350° to 1400°). P. Ya. Saldau, N. A. Zhirnova, and E. L. Klibinskaya. *Keram. Sbornik*, **1939**, No. 4, pp. 24–44.—A chemical investigation showed that in samples of Prosyanovskiĭ kaolin fired at 700° to 850° and treated with NH_4HF_2 the residue represents a substance in which the ratio of $Al_2O_3 : SiO_2 = 1.2$; this shows that metakaolin or anhydride ($Al_2O_3 \cdot 2SiO_2$) is obtained on dehydration. The authors conclude that the exothermic reaction in kaolin at 900° to 1050° is the result of the effect of two reactions: (*a*) the decomposition of metakaolin into a mixture of amorphous $Al_2O_3 + 2SiO_2$ beginning between 850° and 900° and ending between 1050° and 1100° (depending on the rate of heating); with very slow heating for a sufficiently long time, the decomposition of kaolin ends at 900°; (*b*) the crystallization of gamma-Al_2O_3 from amorphous Al_2O_3. An exothermic effect was found between 1200° and 1300° in addition to the two well-known effects; it is a physicochemical constant of the characteristics and nature of kaolin. This reaction has an independent character and always begins after the end of the first exothermic reaction taking place between 900° and 1050°. The temperature of the second exothermic reaction depends on the content of foreign materials; all of these lower the reaction temperature except calcite which has the opposite effect when present in large quantities. The chemical analysis of the residue of all samples in which the third exothermic reaction was eliminated or weakened yielded a ratio of Al_2O_3 to SiO_2 of 3:2, which shows that this reaction, occurring around 1200°, is related to the formation of mullite ($3Al_2O_3 \cdot 2SiO_2$) and not to that of sillimanite ($Al_2O_3 \cdot SiO_2$). M.V.C.

Progress realized in the knowledge of clayey minerals. C. Mira. *Rev. Matériaux Construction Trav. Publics*, No. 359, pp. 87–89B (1939).—Clayey minerals are characterized by (1) a fine particle size which is always below 10 microns and may be below ½ micron; this fineness accounts for the supposition that these minerals are amorphous and is an essential factor which conditions their behavior; (2) a foliated structure of particles; most of the small crystals of these minerals have the form of six-sided lamellas; they crystallize in the monoclinic or rhombohedric pseudohexagonal system; and (3) a crystallized structure arranged in lattices superposed in layers. The most important clayey minerals are classed into five groups: (*a*) The kaolin group consists of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), anauxite (alumina/silica 1 : 3), and kaolinite-anauxite compounds. According to X-ray examination, the following terms which refer to kaolin compounds are synonymous: pholerite (dickite), carnate, newtonite, steinmark, microvermiculite, porcelain clay, porcelain earth (usually kaolinite and halloysite), collyrite, tuesite, arcilla. (*b*) To this group belong montmorillonite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O \cdot nH_2O$), beidellite ($Al_2O_3 \cdot 3SiO_2 \cdot H_2O \cdot nH_2O$), and nontronite ($(Al,Fe)_2O_3 \cdot 3SiO_2 \cdot H_2O \cdot nH_2O$). These minerals have the same lattice structure and the property of swelling when they absorb water and contracting when they lose water. An exact knowledge of the variable nature of these minerals proves that certain terms are unnecessary, e.g., smectite, also known as fuller's earth and bentonite, is montmorillonite. Rock containing montmoril-

lonite together with other impurities is given other names. Nontronite is known by many names, viz., höferite, morencite, mullerite (Larsena and Steiger), faratshite, corencite, pinguite, stilpnochloran (Gruner), chloropal (nontronite and opal), fettbol, hisingerite, and gramenite. (*c*) In this group are halloysite ($Al_2O_3 \cdot 2SiO_2$, $2 + 2H_2O$) and metahalloysite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). Halloysite is distinguished by its two extra molecules of water which are eliminated by heating to 50°. Halloysite is found in kaolin beds with kaolinite (Ross and Kerr). (*d*) This group comprises clayey minerals having the nature of mica (sericite-like minerals). The chemical composition varies between $K_2O \cdot 2H_2O \cdot 3Al_2O_3 \cdot 6SiO_2$ (muscovite) and $^1/_2K_2O \cdot \cdot 2H_2O \cdot 2^1/_2Al_2O_3 \cdot 7SiO_2 + nH_2O$. Unlike normal micas, these minerals have a certain, though limited, capacity for base exchange. Debye-Scherrer diagrams show them to have the same crystalline structure as mica; they lose water in the same manner as muscovite and biotite micas. (*e*) This group comprises clayey minerals with high magnesia concentrations combined in their lattices belonging to the sepiolite-attapulgite series (sepiolite ($2MgO \cdot \cdot 3SiO_2 \cdot nH_2O$), attapulgite ($Al_2O_3 \cdot 4^1/_2SiO_2 \cdot 6H_2O$)). Certain minerals are still classed as problematical, e.g., allophane and leverrierite. Under allophane are grouped all substances which cannot be identified except by radiograph; some are similar in chemical composition to kaolinite and some belong to the montmorillonite group. Recent X-ray studies of the amorphous elements of clays which have been identified with allophane show that these elements are actually crystallized. Hofmann and his collaborators established radiographic diagrams of excess silica and showed that it often exists in clays in the form of cristobalite. The presence of amorphous alumina in clays is also unlikely because it is rapidly transformed into crystalline modifications after its precipitation as hydrate. M.V.C.

Quantitative microchemical analysis of minerals, ores, and rocks: I, Microanalysis of mineral raw materials. I. P. ALIMARIN. *Zavodskaya Lab.*, **9**, 365–71 (1940).—The literature is reviewed. 27 references. **II, Determination of FeO in minerals and rocks.** *Ibid.*, pp. 545–50.—A vanadometric and a photocolorimetric method have been worked out. The latter is based on the reaction of bivalent iron with α-α'-dipyridine to from a red complex $[Fe(C_{10}H_8N_2)_3]x_3$, x being a monovalent complex radical. **III, Determination of water of constitution in minerals and rocks.** *Ibid.*, pp. 983–99.—The Pregl, Friedrich, and Sternberg method of absorbing water in tubes filled with a water-absorbing matter, which is similar to the determination of hydrogen in micro-organic elementary analysis, was investigated and was found to be quite reliable. The apparatus used and the procedure are described in detail. P.B. & E.S.

Recovery of rhodocrosite. ANON. *Chem. Eng. & Mining Rev.*, **33** [389] 133 (1941).—In recovering rhodocrosite from lead zinc ores, a concentrate is prepared by selective flotation and then nodulized, producing a material having 58% manganese. B.C.R.

Refractory clays of the Spirov region. M. M. KUZMIN. *Keram. Sbornik*, **1940**, No. 8, pp. 47–50 (1940).—K. discusses clay deposits and their characteristics and possible uses. M.V.C.

Rock formation: nature's chemical industry. G. W. MOREY. *Chem. & Ind.*, **57** [42] 966–71 (1938); *Chem. Abs.*, **33**, 8535 (1939).—Processes in nature by which many different types of igneous rock and minerals have been formed from a uniform, magmatic mass are outlined and correlated with well-known chemical processes. Fractional crystallization with the separation of crystals from the mother liquor by settling under the influence of gravity or by a squeezing-out process akin to filtration is the chief factor concerned. Other effects are the separation of immiscible liquids, transport of material through a vapor phase, distillation, and sublimation.

Sedimentation of thick clay suspensions. M. B. DONALD. *Trans. Inst. Chem. Engrs.*, **16**, 225–28 (1938); *Brit. Chem. & Phys. Abs.–B*, **58** [9] 937 (1939).—The sedimentation rates for clay slips made from two varieties of Cornish clay in 8 to 15 wt. % concentration have been examined. An accelerated settling rate, just before the critical point is reached, is explained in terms of the colloidal structure of the slip. See *Ceram. Abs.*, **19** [6] 148 (1940).

Sodium bicarbonate (nahcolite) from Searles Lake, California. WILLIAM F. FOSHAG. *Amer. Mineralogist*, **25**, 769–78 (1940).—Sodium bicarbonate was found in large quantities in a well core drilled below the central salt crust of Searles Lake. It occurs in monoclinic crystals and twins, chiefly in a gaylussite marl, and may have been formed either by a reaction between trona and calcium bicarbonate or directly from solution at a time when the lake was a few degrees cooler than at present. W.D.F.

Studies on plagioclase from the diorite porphyry of "Vârful Haitei" (Călimanigebirge, Ostkarpathen). ORESTE NICHITA. *Ann. Sci. Univ. Jassy*, **26** [Part II] 111–21 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 1408.—This plagioclase has a marked zonal structure; in some crystals, over 100 zones were found. The anorthite content found within the crystals decreased toward the surface. Most zones contained 35 to 55% anorthite; the narrow zones contained more anorthite than the wide zones. M.V.C.

Table Mountain lavas and associated igneous rocks near Golden, Colorado. W. A. WALDSCHMIDT. *Quart. Colo. School Mines*, **34** [3] 1–62 (1939).—Three sheets of basalt were extruded in the earliest Eocene time and they now cap these mountains. They originally covered an area of four by ten miles. The source is the Ralston dike, which is the major intrusive in this area. A series of small basalt dikes also occurs here. The essential minerals of the basalt are labradorite, augite, and olivine; accessory minerals are orthoclase, apatite, biotite, and magnetite. Twelve or more zeolites were found in cavities of the basalt, and a list of old analyses is given. W.D.F.

Theory and practice of flotation: I, Development of flotation. RAY W. SCHATZ. *Mines Mag.* [Colo. School Mines], **31**, 9–11, 31 (1941); *Chem. Abs.*, **35**, 1670 (1941).—A discussion of historical development with chronologically arranged data and terminology is presented. 26 references.

Thickness of layers of the dispersing medium in a plastic suspension of mica. M. P. VOLAROVICH AND I. S. EROKHIN. *Zhur. Fiz. Khim.*, **12**, 277–79 (1938).—For muscovite suspensions in vaseline oil, the values of $l_{0\mu}$ (assumption of mica particles in plane parallel layers) and l_μ (assumption that the mica layers occupy 50% of the given planes) for the oil films vary from 13.05 and 6.05μ for a 20% suspension to 4.9 and 1.95μ for a 40% suspension. P.B. & E.S.

Uraninite and thucholite from Pied des Monts, Charlevoix County, Quebec. HUGH S. SPENCE. *Amer. Mineralogist*, **25**, 711–18 (1940).—The age of the uraninite and thucholite is about 900 million years. The pegmatite in which they occur consists predominantly of microcline, with some albite and quartz. Large plates of biotite and muscovite are present, and the muscovite has been mined. Accessory minerals are garnet, beryl, apatite, zircon, monazite, and pyrite. The uraninite has been found in one large pocket and as scattered crystals. It is extensively seamed by the thucholite. W.D.F.

Whitlockite, a new calcium phosphate, $Ca_3(PO_4)_2$. CLIFFORD FRONDEL. *Amer. Mineralogist*, **26**, 145–52 (1941).—Whitlockite is a new mineral which belongs to the rhombohedral division; its habit is also rhombohedral. It was found as a late hydrothermal mineral in pegmatite at the Palmero quarry, near North Groton, New Hampshire. The minerals associated and the sequence of crystallization are whitlockite plus quartz—rhodochrosite—apatite—zeolite. Its physical properties are somewhat similar to those of apatite. W.D.F.

BOOK AND SEPARATE PUBLICATION

Kieselguhr Nacional. S. FRÓES ABREU. Instituto Nacional de Tecnologia, Ministerio do Trabalho, Indus-

tria e Comercio, Rio de Janeiro, 1939, 70 pp.—Several kieselguhr deposits were uncovered along the northern coast of Brazil and in one locality in the southeast near Rio de Janeiro. The uses of kieselguhr are listed in a table and discussed. Flow sheets show the factory preparation of kieselguhr and its application in oil refining. Sketches of the geological occurrence of the several deposits, the chemical analyses, etc., are given and discussed. Photographs of the deposits and good microscopic magnifications of kieselguhr are included. T. W. GARVE

Pictou Coalfield, Nova Scotia. W. A. BELL. *Geol. Survey, Bur. Geol. & Topography, Mines & Geol. Branch, Dept. Mines & Resources, Canada, Pub.* No. 2457 (1940). 170 pp., 10 plates, 1 map, 1 diagram. Price, paper, 50¢.—The bulk of this report is devoted to coal stratigraphy, structural geology, and economic geology of coal of the Pictou field. Building brick, firebrick, sewerpipe, and various vitrified or glazed products are made by two companies from local clays. G.M.H.

PATENTS

Froth flotation process. W. T. BISHOP (Hercules Powder Co.). U. S. 2,238,439, April 15, 1941 (July 25, 1939).—A process for the froth flotation of negatively charged minerals comprises frothing an aqueous suspension of the minerals in the presence of a reaction product of chlorinated paraffin hydrocarbons having between 22 and 30 carbon atoms and ammonia, the product having a positively charged surface active ion.

Obtaining soluble beryllium compounds starting from ores containing beryllium. CARLO ADAMOLI (Perosa Corp.). U. S. 2,238,206, April 15, 1941 (July 17, 1937).

Purifying molybdenite concentrates. C. H. CURTIS (Miami Copper Co.). U. S. 2,238,250, April 15, 1941 (May 26, 1939).

Recovery of fluorspar from ores. N. L. SHEPARD (Aluminum Co. of America). U. S. 2,238,662, April 15, 1941 (April 19, 1939).—In the process of floating fluorspar values from fluorspar ore, the steps comprise creating a fluorspar-lifting froth from a pulp containing a collector including a fatty acid radical, the pulp having a pH greater than about 9, collecting and repulping the froth, acidifying the pulp to give a pH less than about 7, and creating therefrom another fluorspar-lifting froth which is substantially free from calcite.

Chemistry and Physics

Binary system MgO–B_2O_3. N. A. TOROPOV AND P. F. KONOVALOV. *Zhur. Fiz. Khim.*, **14**, 1103–1109 (1940).—Heating and cooling curves of sintered mixtures of chemically pure MgO and B_2O_3 were determined. The crystallization products were studied optically and by X-ray analysis by the Debye-Scherrer method. P.B. & E.S.

Chemical analysis of chromites. N. V. LAZAREV. *Zavodskaya Lab.*, **9**, 152–57 (1940). P.B. & E.S.

Chromium ore: IV. K. KONOPICKY AND F. CAESAR. *Ber. Deut. Keram. Ges.*, **21** [1] 18–20 (1940).—Highly concentrated phosphoric acid (density 1.9), which contains some vanadium pentoxide, quickly dissolves chromium ore as well as calcined ore and chromium oxide. The acid mixture permits a quick and accurate determination of the FeO content of the chromium ore, slags, etc., without use of a stream of carbon dioxide. For Part III see *Ceram. Abs.*, **20** [4] 95 (1941). W.H.H.

Determination of chrome in acid slags. S. V. BUDAEV AND P. I. SHPORTENKO. *Zavodskaya Lab.*, **9**, 1038 (1940).—Instead of being fused with sodium peroxide with a subsequent separation of the precipitate, the sample is dissolved in a sulfophosphoric mixture, 15 ml. H_3PO_4 (1.70) + 85 ml. H_2SO_4 (1:4) in the presence of 2 to 3 gm. of fluorite. Vd can then be determined without any separate fusing together. P.B. & E.S.

Determination of free lime in Portland cement. E. SPOHN. *Zement*, **29** [17] 205–207 (1940).—Small specimens of the raw mix are wetted and formed into balls 17 mm. in diameter and fired for 30 min. at 1450°C. A modification of Emley's titration method requiring only 20 min. is described. F.E.S.

Determination of silicic acid. HIDEHIRO GOTO. *Science Repts. Tôhoku Imp. Univ., Series 1*, **29**, 440–45 (1940).—In an attempt to avoid double evaporation in the determination of silica, G. found that the silicic acid in the residue, after being heated for 1 hr. at 130°C., remained insoluble when treated with 15 ml. glacial acetic acid, later diluted to about 60 ml. Aluminum and iron go into solution and do not interfere. Filter papers soaked in collodion were found to be satisfactory for filtering many types of colloidal solutions. W.D.F.

Electrochemical theory of slag-metal equilibria: I, Reactions of manganese and silicon in acid open-hearth furnace. P. HERASYMENKO. *Trans. Faraday Soc.*, **34**, 1245–54 (1938); *Chem. Abs.*, **33**, 2039 (1939).—From analyses of slag and metal in the temperature range 1550° to 1640°, the following empirical constants were found: $K_{Mn} = (FeO)\,[Mn]/(MnO)$, $K'_{Si} = (FeO)^2 \cdot [Si]$, $K'_{SiMn} = (MnO)^2 \cdot [Si]/[Mn]^2$. These constants are sufficiently accurate for practical steel making and may be employed for the calculation of the contents of some constituent in steel or slag in the period of a heat when the bath is boiling moderately and the total amount of slag is not excessively high. From the assumption that, in liquid acid slag, electrolytic dissociation is complete and there are no electroneutral molecules present, a general theory of the equilibrium in the acid slag–steel system is developed. It is concluded that SiO_2 present in acid slags in excess of the amount necessary to form molten salts of the type $R_2^{II}SiO_4$ is completely dissociated according to the equation $2SiO_2 \rightarrow Si^{4+} + SiO_4^{4-}$. **II, Reactions of Cr in the acid open-hearth furnace.** *Trans. Faraday Soc.*, **34**, 1254–57 (1938).—The equilibrium constants for the reactions of Cr in liquid steel with acid slags were determined from the data on five acid open-hearth heats. Based on the electrochemical principles developed in Part I, the relative activity coefficient of Cr in liquid steel was found to be equal to the equilibrium constant $K_{Mn,Cr} = (CrO)[Mn]/(MnO)[Cr]$. A parallelism was shown between the vapor pressure of elements and the relative electrochemical activity coefficient of these elements dissolved in liquid Fe.

Fluoride: lanthanum acetate as reagent. J. FISCHER. *Z. Anal. Chem.*, **104**, 344–46 (1936); abstracted in *Analyst*, **61**, 436 (June, 1936).

Geometrical factors in reactions involving solids. J. D. BERNAL. *Trans. Faraday Soc.*, **34**, 834–39 (1938); *Jour. Soc. Glass Tech.*, **22** [93] 299A (1938).—In all solid reactions there is a tendency to preserve crystal orientation and atomic positions as little changed as possible. Polymorphic transformation may be sharp, as in the α-β quartz change, or extremely sluggish, as in the change of quartz to tridymite which involves the breaking of silicon-oxygen bonds. Reference is made to the structural changes which take place in the dehydration of Fe, Al, and Mn hydroxides and to the absorption of water by zeolites. AlF_3 has a structure which contains separate cavities in which water is trapped during crystallization. This water can be driven off only at 1000°.

Heterogeneous reaction between chromic sulfate and manganese dioxide. MATA PRASAD, M. A. NAQVI, AND V. N. SHETGIRI. *Current Sci.*, **8** [8] 361–62 (1939).—When a solution of chromium sulfate is shaken with solid manganese dioxide, dichromate ions are formed in the solution. The reaction takes place as follows: $Cr_2(SO_4)_3 + 3MnO_2 + H_2O = 3MnSO_4 + H_2Cr_2O_7$. The authors found that (1) the gram molecules of the dichromate ions formed in the reaction are equal to those of the chromium sulfate used up and (2) the ratio of the gram molecules of manganese sulfate to those of dichromate formed is nearly equal to 3. A.P.S.

Improved technique for mounting powdered samples for X-ray diffraction. J. S. LUKESH. *Rev. Sci. Instruments*,

11 [6] 200–201 (1940).—Cylinders of powder used for X-ray photographs are made by extrusion from a nozzle. The principle is the same as that of the ordinary grease gun, only on a much smaller scale. Binders are necessary, and library paste or collodion diluted with an equal amount of amyl acetate gives satisfactory results. This procedure gives samples of uniform size and reduces background scattering. H.E.S.

Mechanism of reactions of the type solid = solid + gas. J. ZAWADSKI AND S. BRETSZNAJDER. *Trans. Faraday Soc.*, **34**, 951–59 (1938); *Jour. Soc. Glass Tech.*, **22** [93] 298A (1938).—In the system solid = solid + gas, spurious equilibria are easily obtained. An extreme case is furnished by zinc carbonate, and synthesis from ZnO and CO_2 has not yet been accomplished. The decomposition and formation of $CdCO_3$ is a second example; with repeated decomposition and reformation through CO_2 pressure variation, the rate of reaction becomes zero at pressures $p > p_0$ in the case of synthesis and $p < p_0$ in the case of dissociation (p_0 is the dissociation pressure). The difference between p and p_0 increases with the number of successive operations owing to increasing crystal regularity and consequent lower velocity of nucleus formation. In the case of mobile systems, spurious equilibria of another type may occur, e.g., if the formation of carbonate from CaO and CO_2 commences at pressures considerably exceeding p_0 there is a spurious equilibrium at $p > p_0$, owing to the formation of small crystals. In time, as recrystallization proceeds, the equilibrium pressure tends to p_0. In the ideal case the reaction velocity, v, $= k(p - p_0)$, where k is independent of temperature. If $p_0 > p$ there is dissociation, and if $p_0 < p$, synthesis of carbonate. The rate of decomposition of single calcite crystals varies according to the origin of the crystals owing to the fact that the structural irregularity may vary.

Potentiometric determination of aluminum in ores and silicates. V. F. STEFANOVSKIĬ AND V. D. SKIRENKO. *Zavodskaya Lab.*, **9**, 1151–53 (1940).—The Tarayan method (see following abstract) of potentiometric titration of Al with sodium fluoride was checked and was found to be suitable for quick and sufficiently accurate determinations of Al in silicates. The method has been slightly modified and simplified. Its disadvantages include a sudden small increase of potential at the equivalent point and its limitation by the ratio of Al_2O_3:Fe_2O_3 in the sample. P.B. & E.S.

Potentiometric titration of aluminum in silicate rocks. V. M. TARAYAN. *Zavodskaya Lab.*, **8**, 273–76 (1939); *Chem. Abs.*, **34**, 43 (1940).—Fuse 0.25 to 0.30 gm. of the sample with Na_2CO_3, dissolve in HCl, precipitate the Ti, Al, and Fe with NH_3, filter, wash with hot water, and dissolve in 1 *N* HCl until acid to methyl orange. Saturate the solution with NaCl, add an equal volume of alcohol, saturate with CO_2, add 3 to 4 drops of cold saturated $FeSO_4$ solution, and titrate with 0.5 *N* NaF. The potentiometric results are as accurate as gravimetric results. See preceding abstract.

Rapid determination of silica in Portland cement. A. STEOPOE. *Zement*, **29** [16] 193–94 (1940).—The cement is decomposed with HCl in the presence of an organic colloid such as gelatin or agar-agar. See "Determination . . .," *Ceram. Abs.*, **19** [7] 153 (1940). F.E.S.

Surface tension in binary and ternary oxide mixtures. P. P. KOSAKEVICH AND A. F. KONONENKO. *Zhur. Fiz. Khim.*, **14**, 1118–27 (1940).—In general, lime increases the surface tension of iron slags, presumably because it combines with the silica accumulating in the surface layer, resulting in a surface-inactive silicate and a fall of the silica content in the superficial slag layer. In FeO-MnO-SiO_2 mixtures, however, the surface activity of SiO_2 is practically independent of the FeO:MnO ratio in the mixture. P.B. & E.S.

General

Accuracy of fluoroscopy in detection of pulmonary tuberculosis. H. L. ISRAEL AND H. W. HETHERINGTON. *Amer. Jour. Med. Sci.*, **201**, 224–32 (Feb., 1941).—Fluoroscopic examination by physicians with limited training and experience in fluoroscopy should detect, in diagnostic practice or in mass surveys, almost all tuberculosis infiltrations of immediate clinical significance. In the present series of approximately 1000 duplicate examinations, in only four instances were significant lesions of this type not recognized. Results satisfactory for clinical purposes were obtained even in obese patients. Smaller tuberculous lesions of questionable clinical significance but of considerable importance in epidemiologic investigations were frequently overlooked by physicians without special training. Individual variations in accuracy among the 18 physicians studied were accounted for by their failure to wait for adequate dark adaptation. The results of fluoroscopic and film examination in the diagnosis of tuberculous tracheobronchial lymph node enlargement corresponded closely. Inconsistent results were given by these two methods in the diagnosis of calcified primary lesions. F.S.M.

American ceramics in 1940. ARTHUR S. WATTS. *Ohio State Univ. Eng. Expt. Sta. News*, **13** [1] 21–22 (1941).—Refractories are closely connected with national defense. There has been steady production and an increase in quality. Better chemical stoneware helps chemical processes. Every new army camp will need sanitary ware, drain tile, sewer pipe, brick, Portland cement, and dishes. A new all-alumina spark plug is molded with a synthetic resin, and the resin is then burned out at extreme temperatures. This plug meets all service requirements for both automobiles and airplanes, including large bombers. W.D.F.

Ceramic batches. ANON. *Ceram. Ind.*, **35** [4] 112–21 (1940).—A representative collection of batch recipes used in industry to prepare a wide variety of enamels, glasses, pottery bodies, and glazes is presented. A.F.M.

Ceramic calculations. ANON. *Ceram. Ind.*, **35** [4] 122–28 (1940).—The theory of common ceramic calculations is worked out. Typical examples illustrate the procedure necessary in computing pottery, glass, and enamel batches. A.F.M.

Ceramic materials. ANON. *Ceram. Ind.*, **35** [4] 12–85 (1940).—A description is given of the physical and chemical properties, uses, and effects of over 300 materials used in the manufacture of enamel, glass, and pottery products. A.F.M.

Dust utilization—dust dangers. FRITZ GEHRMANN. *Gasmaske*, **11**, 131–36 (1939).—Money losses in various industries by undesired dust formation are discussed. Silicosis is also discussed briefly. Protection against it is afforded by the use of dust masks. Eleven illustrations show the use of the dust mask in many industries. W.D.F.

Engineering control of dust with special reference to respirators. A. D. BRANDT. *Bull. Amer. Ceram. Soc.*, **20** [4] 122–25 (1941).

Fit for the job. S. F. MEEK. *Nat. Safety News*, **42**, 33–34, 62 (Aug., 1940).—M. outlines pre-employment examination and gives principles which will provide the physician with an opportunity to exert the greatest possible influence in the safe placement of new employees. It is suggested that the routine physical examination be supplemented by various psychological or psychiatric tests to determine particular job aptitude, reaction time, memory, temperament, mental capacity, and emotional stability. F.S.M.

Flocculation and settling characteristics of fine dusts. ANON. *Chem. Eng. & Mining Rev.*, **33** [389] 136 (1941).—Dusts suspended in air undergo a change in composition as settling proceeds. In investigating dusts capable of producing silicosis, the composition of the dust inhaled cannot be assumed to be identical with that of the rock being mined. Certain minerals have a flocculating effect on other minerals, thus promoting settling. In tests on various minerals using a tyndallmeter, impure quartz and sericite showed the slowest settling rates. The addi-

tion of calcined gypsum to quartz dusts greatly increased the settling rate, as did limestone, but to a lesser degree. B.C.R.

Health activities pay out. H. C. BEAVER. *Occupational Hazards*, **3**, 21–22 (Feb., 1941).—With the installation of a health program costing a total of $6445 a year, a typical company employing 500 employees saved $10,451, leaving a net savings to the company of $4006. In addition to this saving, the employees, because of fewer absences, received $5040 more annually in pay. Thus, the operation of a health program in the smaller sized companies, in addition to its humanitarian value, makes an actual financial contribution to the workers and the management. F.S.M.

Health of brick and tile plant workers in North Carolina. M. F. TRICE. *Bull. Amer. Ceram. Soc.*, **20** [4] 130–34 (1941).—10 references.

Physical examinations in employment: II, From the legal viewpoint. T. C. WATERS. *Proc. All-Ohio Safety Congress, 11th Congress*, pp. 342–47 (1940).—In the absence of statutory prohibition, an employer has the legal right to request an employee to subject himself to physical examination as a prerequisite for accepting him for employment; he does not, however, have the affirmative right, except by statutory provisions, to require an employee to submit to periodic post-employment examination. The legislative provisions on this subject are discussed at length, especially the Wisconsin program. W. states that plans for the physical examination of employees exposed to industrial hazards will become an essential part of the successful administration of our workmen's compensation laws. F.S.M.

Point plan for rating jobs. N. G. MILLS. *Factory Management & Maintenance*, **98** [12] 61–68 (1940).—M. presents a detailed plan for rating jobs in industrial plants. He considers that skill, effort, and working conditions characterize the job. Skill and effort factors are broken down into (1) blueprints, (2) setups, (3) difficulty, (4) accuracy, (5) responsibility, and (6) variation. Working conditions are divided into ten elements: (1) accident hazard, (2) fatigue, (3) eyestrain, (4) heat, (5) cold, (6) acids, (7) dirt or dust, (8) weight, (9) fumes, and (10) wet. Point ratings are assigned to each factor and element. Tables containing the number of points allowed for each degree of each element are presented with a full explanation for each rating. J.L.G.

Recent legislation on occupational diseases. THEODORE C. WATERS. *Bull. Amer. Ceram. Soc.*, **20** [4] 126–30 (1941).

Research and social progress. C. F. KETTERING. *Mech. Eng.*, **58** [4] 211–14 (1936); abstracted in *Bull. Brit. Non-Ferrous Metals Research Assn.*, No. 87, p. 23 (1936).

States of dust. O. BRANDT. *Kolloid-Z.*, **85**, 24–32 (1938); *Science Abs.-A*, **41** [492] 1103 (1938).—B. describes three states in which dust may exist: (1) suspended in a gas (*schwebezustand*), $k = 1$; (2) as a self-supporting structure with no part of the weight carried by the gas (*lagerzustand*), $k = 0$; and (3) in a state of flow in which part of the weight of the dust is borne by the gas (*fliesszustand*), $0<k<1$. These states are defined by the value of the flow factor (k), the fraction of the total weight of dust which is carried by the gas. An account is given of an experimental investigation of states 2 and 3. H.K.R.

BOOKS

Accident and Health Insurance. EDWIN J. FAULKNER. McGraw-Hill Book Co., Inc., New York, 1940. 366 pp. Price $4.00.—This book brings together for the first time material most of which has never before been published and much of which was widely scattered and unavailable to the average interested reader. Of particular interest are the sections on employers' liability and workmen's compensation insurance. F. outlines the progressive change from the old English common law of master and servant to the passage of the employers' liability acts whose purpose was to increase the responsibility of the employer for industrial injuries sustained by his employees. The opportunity arose for insurance coverage which would protect the master in the event of a suit by his servant, as a result of which the employers' liability policy was developed. These acts have, to a large extent, been superseded by compensation acts and have a significant application only in the two states which do not have compensation acts and in connection with employment excluded from the compensation laws of the other 46 states. Workmen's compensation insurance is discussed with very little reference to occupational disease coverage. The subject of accident and health insurance in its general aspects is dealt with. An index and an appendix containing examples of the various policies are included. F.S.M.

Public Health Administration in the United States. WILSON G. SMILLIE. Macmillan Co., New York, 1940. 2d ed. 553 pp. Price $3.75.—The appearance of the second edition of this text, five years after the first, is a recognition of the rapid growth and expansion of public health administration in this country. The Social Security Act of 1935 evidenced an awakened public interest in national health affairs. F.S.M.

Symposium Dedicated to I. V. Stalin. Academy of Sciences of the Ukrainian S. S. R., Kiev, 1940. **Silicate Industry in Stalin's Five-Year Plans.** P. P. BUDNIKOV. Pp. 541–56.—B. gives a brief account of the economic and technical development of the silicate industry of the Soviet Union during the last decade. P.B. & E.S.

PATENT

Manufacture of ceramic products. N. S. GARBISCH. Brit. 533,968, March 12, 1941 (Sept. 7, 1939).

TENTATIVE STYLE SHEET FOR PUBLICATIONS OF THE AMERICAN CERAMIC SOCIETY*

abscissa abscissas (pl.)
absolute (temperature) abs. or °K
acidproof (n. and v.)
A.D. 1900 (not 1900 A.D.)
aftereffect
afterexpansion
aftershrinkage
afterward (not afterwards)
aging (not ageing)
air blast
air conditioning; air-conditioned (adj.)
air-cool (v.); air-cooled (adj.); air cooling (n.)
air-set
airtight
align (not aline)
alkali alkalis (pl.)
alpha-alumina
alternating current a.c. a.-c. (adj.)
alumino (usually one word as compound)
aluminum (not aluminium)
Alundum (trade name)
ampere(s) amp.
an (do not use before words starting with long u sound)
analyze (not analyse)
angstrom unit a.u.
anti- (usually one word as compound)
apparatus (sing. and pl.)
approximately (in tables, approx.; do not abbreviate in text)
arch brick (n.); arch-brick (adj.)
archeology
artware
as regards (do not use)
association Assn. (not Assoc.)
atmosphere(s, ic) atm. (in abstracts and tables only)
atomic weight at. wt. (in tables)
average avg. (in tables)

backup (n.); back up (v.)
Bakelite (trade name)
balance (never use in the sense of remainder)
barite native barium sulfate, $BaSO_4$
baryta barium monoxide, BaO
barytes mineral, barite
base exchange (n.); base-exchange (adj.)
base metal (n.); base-metal (adj.)
bathtub
Baumé Bé.
B.C. follows numeral (104 B.C.)
blowhole
blowpipe
border line (n.); borderline (adj.)
breakup (n.); break up (v.)
brick (usually singular)
brickmaking
brickwork, brickworks
Brinell
briquette (not briquet)
British thermal unit B.t.u.
build-up (n. and adj.); build up (v.)
Bunsen burner
burette (not buret)
by (in Journal and Bulletin papers spell out in text; in tables and abstracts use 2 x 4 x 8 in.)
bylaws
by-pass (n., v., and adj.)
by-product

calorie (small) cal.
calorie (large) Cal.
cannot
Carborundum (use silicon carbide, except where specific trade product is meant)
cast iron (n.); cast-iron (adj.)
catalogue
Centigrade C.
century (never capitalize)
champlevé (not italic)
checker-brick (n. and adj.)
checkerwork
chemically pure c.p.
chemico (usually one word as compound)
chinaware
clayware
clay working (n.); clayworking (adj.)
cloisonné (not italic)
coal gas
cone 1 (not capitalized)
conveyer (not conveyor)
cooperate
coordinate
copperhead
councillor
counterclockwise (adj. and adv.)
crankpin
cross bending
cross section (n.); cross-section (adj. and v.)
crossed Nicols
cryolite (not kryolite); Kryolith, trade name
cubic centimeter(s) cc.
cubic meter(s) cu. m.

dead-burn
deair
debris (no accent)
de-enamel
deflocculant
degree (spell out without numeral; otherwise 6 °C., 6 °F.)
delftware
density d (d_4^{15}, density is for 15 °C. referred to water at 4 °C.)
dew point
diaspore (not diaspor)
Dinas clay; Dinas brick
dinnerware
direct current d.c. d.-c. (adj.)
direct-fired (adj.)
disk (not disc)
downdraft
draft (not draught)
drier (not dryer)
dry-press (v. and adj.)
dust-counter
dustproof

earthenware
electro (usually one word as compound)
electromotive force e.m.f.
electroosmosis
enameled, enameling (one l)
enamelware
end point
et alii et al. (italic)
et cetera etc. (not italic)

face brick (n.); face-brick (adj.)
Fahrenheit F.
faience (not fayence)
feed water (n.); feed-water (adj.)
feldspar (never use "spar" alone, except as heavy spar)
fiber (not fibre)
figure fig. (spell out at beginning of sentence)
filter press (n.); filter-press (v.)
fire bed
firebox
firebrick
fire bridge
fire clay (n.); fire-clay (adj.)
fire-cracking
fire hearth
fireplace
fire pocket
fireproof
fire resistance
fire travel
fish scale (n.); fish-scale (v.)
flash wall
flowerpot
flowmeter
flowsheet
foot-pound(s) ft.-lb.
for example e.g. (not italic)
forehearth
formula formulas (pl.)
frit (not fritt); fritted, fritting
fulfill
fuller's earth

gauge (not gage)
glass blower, glass blowing
glass cutting
glassforming
glass gall
glasshouse
glassmaker, glassmaking
glassmelting
glass painting
glass pot
glassteel
glassware
glassworker, glassworking, glassworks
Glauber's salt
Globar (trade name)
glucinum (beryllium)
gooseneck
grain(s) gr.
gram(s) gm. or spell out
gram-calorie (same as calorie (small))
gray (not grey)
grayware
greater than >
groundmass

hairline
handmade
hand press
heat balance (n.); heat-balance (adj.)
heat-treat (v.); heat-treatment (n.)
high lights
hollow ware (n.); hollow-ware (adj.)
horsepower h.p.
hour(s) hr. (not hrs.); abbreviate only in tables and abstracts
hydrogen ion (n.); hydrogen-ion (adj.)

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* Webster's New International Dictionary, Second Edition, Unabridged, has been followed wherever possible in preparing this style sheet.

hydrogen-ion concentration pH
hyphens (compound modifiers ending in "ly" should not be hyphenated)

inasmuch as
index { indexes (pl.) in regard to subject, author, etc. / indices (pl.) mathematical, refractive indices }
index of refraction n
infrared (adj.)
inter (usually one word as compound)
interrelate
in vacuo

°K. degrees Kelvin or absolute
kilo (one word as compound)
kilocycle(s) kc.
kilogram-calorie (same as calorie (large))
kilovolt(s) kv.
kilovolt-ampere(s) kva.
kilowatt(s) kw.
kilowatt-hour(s) kw.-hr.
knife-edge
kyanite (not cyanite)

lamella lamellas (pl.); lamellar (adj.)
Le Châtelier's law
lehr (not leer)
less than $<$
lightweight
limekiln
limewater
liquefaction
liquefy (not liquify)
liter (not litre); always spell out
logarithm { log or $\log_{10}$ Briggsian logarithm / ln or $\log_e$, natural or Napierian logarithm }

machinability
make up (v.); make-up (n. and adj.)
Mariotte's flask or bottle
mat (not matt or matte), meaning dull surface
matte (metallurgical term)
medieval (not mediaeval)
Méker burner
metalware
mho unit of conductance
micelle micelles (pl.)
micro (usually one word as compound)
microammeter
microgram(s) μgm.
micromicron(s) $\mu\mu$
micron(s) μ
microphotograph (small photograph)
milliequivalent(s) m.e.
milliliter(s) ml.
millimeter(s) mm.
millimicron(s) mμ
millivolt(s) mv.
modeling, modeler (one l)
Mohs' scale
mol (no period) or mole gram molecule
molal
molar
mold (not mould)
molecular weight mol. wt. (in tables and abstracts)
molecule mol. (do not confuse with mol or mole, gram molecule)
mono (usually one word as compound)
multi (usually one word as compound)

namely viz. (not italic)
Nichrome (trade name)
non (usually one word as compound)
normal N

open hearth (n.); open-hearth (adj.)
over (usually one word as compound)
over-all (adj.)
oxidize (not oxidise)

page p.; pages pp.
partial derivative ∂
parts per million p.p.m. (in tables and abstracts)
peephole
per (use / in tables only)
per cent (use % with numbers)
pH measure of hydrogen-ion concentration
phase difference
photo (all one word as compound)
photomicrograph, photograph of microscopic image; (distinguish from microphotograph)
physico (usually one word as compound)
pinhole (n. and v.)
pipette (not pipet)
plaster of Paris
platinum-platinum rhodium Pt-Pt Rh
poise, c.g.s. unit of absolute viscosity
Poisson's ratio
Portland cement
pozzuolana
pre (one word as compound except as in pre-Cambrian)
pressed ware
proved (preferred to proven)
pug mill
Pyrex-brand glass (not Pyrex glass)

quicklime

radioactive
re-employ
refire
regime (no accent)
reinforce (not reënforce)
re-press (use hyphen meaning to press again)
résumé
revolutions per minute r.p.m.
role (accent not required)
Roentgen ray (X ray)
roentgenize, roentgenograph, roentgenology
run of mine; run-of-mine (adj.)

salt cake
salt glaze, salt glazing; salt-glazed (adj.)
saltpeter
sandblast
sanitary ware
sea water
semi (usually one word as compound)
setup (n.); set up (v.)
Sèvres
sewer pipe (n.); sewer-pipe (adj.)
shatterproof
sheet iron (n.); sheet-iron (adj.)
shutdown (n.); shut down (v.)
shutoff (n. and adj.); shut off (v.)
silex (not capitalized when referring to silica composed essentially of quartz)
siliceous (not silicious)
silico (usually one word as compound)
silicon carbide (see also Carborundum)
siloxicon
skewback
skillful
soft-mud (adj.)
soundproof (v. and adj.)
spar (never use alone, except as "heavy spar")
specific gravity sp. gr. (in tables only)
specific volume sp. vol. (in tables only)
stiff-mud (adj.)
Stokes' law
stoneware
stopcock
streamline
sub (one word as compound)
sulfur, sulfide, sulfate (not sulphur, sulphide, sulphate)
super (one word as compound)

tableware
teapot
technique (not technic)
terra cotta (n.); terra-cotta (adj.)
test piece
textbook
that is i.e. (not italic)
thermo (usually one word as compound)
though (not tho)
through (not thru)
time limit
times (use $\times$); by (use x)
ton (spell out)
toward (not towards)
trademark (n. and v.)
traveled, traveling (one l)
tri (one word as compound)
truing (not trueing)
tuyère

ultraviolet (adj.)
under (one word as compound)
updraft (n. and adj.)
up-to-date (adj.; otherwise not hyphenated)
upward (not upwards)

Vallendar clay
versus vs. (not italic)
via (not italic)
vice versa (not italic)
volt-ampere
voltmeter

ware (not wares)
water bath
water-cool
water gas (n.); water-gas (adj.)
water gauge
water glass (n.); water-glass (adj.)
water jacket (n.); water-jacket (v.)
water power (n.); water-power (adj.)
waterproof, waterproofing
water smoke (n.); water-smoke (v.)
water-soak
water tank
watertight
water vapor
watt-hour (spell out)
wattmeter
wave length
Wedgwood (not Wedgewood)
weight loss
wellhole
well known; well-known (adj.)
whiteware
workpiece

X radiation
X ray (n.); X-ray (adj. and v.)

yield point

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